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Fuel for Firefighting Foam Evaluations: Gasoline vs Heptane

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14. ABSTRACT

Gasoline and heptance pool fire extinctions have been comparatively evaluated with AFFF and fluorine-free formulations at a benchtop scale. The AFFF formulations are relatively insensitive to the identity of the fuel, but the F3 formulations display significant divergence in extinction capability, with the gasoline fire being the more difficult to extinguish. Individual major components of gasoline were tested, and the aromatic components were determined to be the source of this difficulty in gasoline fire suppression. Within the aromatic components, this effect substantially increased with the number of methyl substituents (trimethylbenzene > xylenes > toluene > benzene). This aromatic gasoline component effect correlated with extraction of surfactants across the water-fuel interface and in the same order of aromatic compound effectiveness. A trimethylbenzene-heptane mixture is similar to gasoline with respect to F3 formulation fire extinction, foam degradation, and fuel vapor transport measurements. This mixture is proposed for consideration as a standard fuel for F3 concentrate fire suppression testing in place of complex and variable gasoline compositions.

15. SUBJECT TERMS

AFFF	Fluorine free foam (F3)	MIL-F-24385F
Gasoline	Heptane	Pool fire extinction

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EXECUTIVE SUMMARY

Aqueous film-forming foams (AFFF) are used to rapidly extinguish fuel fires and are generated from commercial surfactant concentrates whose use in the military requires evaluation for MilSpec compliance. AFFF formulations include fluorocarbon surfactants which are their most active component. The unique properties of these surfactants (low surface tension, hydrophobicity, oleophobicity, thermal stability) enable their formulations to form aqueous films and foams that spread very rapidly on burning hydrocarbon fuel surfaces, function as a very stable and excellent barrier to permeating hydrocarbon fuel vapors and thermally insulate the fuel surface from the combustion above. Since 2000, use of these fluorocarbon surfactants has been increasingly limited due to bioaccumulation and toxicity. In recent years research efforts have been initiated to develop fluorine-free foams (F3) to be used in place of AFFF for hydrocarbon pool fire suppression, and commercial F3 concentrates are becoming available. While these commercial F3 formulations have yet to receive qualification under the current MilSpec (MIL-F-24385F), a new version is under consideration (Mil-PRF-24385G) where a proposed change in fuel from alcohol-free gasoline to heptane is being considered. The work summarized in the next paragraph and reported in this report originated from a research project focused on developing an F3 formulation with pool fire suppression capabilities comparable to AFFF. During the course of experimentation, it was observed that the research F3 formulations' capability for extinguishing gasoline pool fires was considerably less than that for heptane fires. Experimentation with commercial F3 formulations revealed a similar but variable and less pronounced effect. The results summarized in the following paragraph and described in this report are intended for consideration in the MilSpec revision process.

This research project has focused on development of a F3 formulation based on a combination of polyoxyethylene-siloxane surfactants with alkyl polyglucoside surfactants and has achieved a benchtop heptane pool fire extinction result that is within 60% of a MilSpec qualified AFFF formulation. Advancement of this experimental F3 formulation to the MilSpec 28 ft^2 gasoline pool fire suppression testing resulted in no extinction instead of the anticipated 30-60 second extinction time. Subsequent testing revealed that this divergent result was attributable to the identity of the fuel, and a subsequent 28 ft^2 heptane pool fire suppression test resulted in a 50 sec extinction time consistent with benchtop testing. Further benchtop experimentation found that the aromatic components in gasoline had a detrimental effect on achieving pool fire extinction, and, within these aromatic components, there is a correlation between the degree of extinction resistance and methyl substitution on the aromatic compound (trimethylbenzene > xylenes > toluene > benzene). It was further found that the mechanism involved extraction of an F3 surfactant component into the fuel. As a potential useful application of this knowledge, it is proposed that simple and well-defined two-component simulant for gasoline, a trimethylbenzene/heptane mixture, could be developed for gasoline sensitivity testing of F3 formulations to diagnose extinction shortfalls that heptane pool fire testing will not detect.

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FUEL FOR FIREFIGHTING FOAM EVALUATIONS: GASOLINE VS HEPTANE

INTRODUCTION

The use of foam to extinguish fuel fires has a history dating back to the early 1900's [1], and today foam plays this critical role at fuel storage areas, airports, military bases and ships. In the 1950's electrochemical fluorination technology provided an economical route to perfluoro surfactants which in foam formulations proved superior to the then-in-use protein foams. A brief history of this surfactant development is provided in the paragraphs below. The unique properties of the perfluorinated surfactants (low surface tension, hydrophobicity, oleophobicity, thermal stability) enabled their formulations to form: (1) aqueous films that spread on liquid hydrocarbon fuel surfaces, (2) stable foams with excellent barrier properties to permeating hydrocarbon fuel vapors, and (3) thermally stable and insulating foam barriers between the flame above and the pool surface below the burning fuel. After over 40 years of using fluorocarbon surfactants in fire suppressing foams, toxicity effects attributed to the presence of these surfactants in the environment, particularly ground water, has resulted in a restriction and, possibly in the future, an elimination of their use in this application. Currently, research programs are seeking to develop fluorine-free surfactant foam formulations that will extinguish fuel fires with an effectiveness equivalent to the fluorosurfactant containing formulations. This equivalent effectiveness is determined by specifications from various organizations which include the Department of Defense (MilSpec – MIL-F-24385F), European Committee for Standardization (EN1568-Part 3), Underwriters Laboratory (UL162), International Civil Aviation Organization (ICAO-Level C) and National Fire Protection Association (NFPA 11 2016). The testing protocols set forth by these organizations vary in severity of evaluation tests for foam formulation product qualification. The MilSpec standard is the most rigorous, and at present no fluorine-free surfactant formulation product has received its qualification. One of the unique aspects of the current MilSpec testing is its use of alcohol-free gasoline as the fuel in pool fire extinction testing. Most other protocols use heptane(s) or a diesel fuel. In our research to develop a fluorine-free surfactant foam formulation, we find a significant difference in effectiveness for extinguishing pool fires depending on whether gasoline or heptane are used as the fuel. In addition to experimental formulations, this observation is also made for a series of commercial fluorine-free foam formulations. However, this gasoline-heptane fuel difference effect is nearly insignificant when fluorosurfactant containing foam formulations are used. The intent of this report is to circulate these results to interested parties as constructive input. With the current 2017 version of MilSpec (MIL-PRF-24385F) undergoing revision and a changing of the pool fire fuel from gasoline to heptane being considered, it is thought that the information reported here may be of interest.

History. The intent of this brief subsection is to provide a perspective on the evolution of fluorocarbon surfactants. It is thought to be very useful toward understanding how and why certain fluorosurfactant related compounds – particularly perfluorooctanoic acid (PFOA) and perfluorooctylsulfonic acid (PFOS) evolved to the position in which they are now. For a rapid reading of this report focused only on recent experimental evidence depicting a divergence in fire

suppressing performance of fluorine-free surfactant foam formulations between gasoline and heptane, this section may be skipped.

The development of fluorocarbon chemistry was much accelerated by its incorporation into the Manhattan Project during WWII [2]. Critical operations in this project were the transformation of uranium ore into uranium hexafluoride and then the concentrating of the radioactive ^{235}U isotope via processes of gaseous diffusion, liquid thermal diffusion or centrifugation. UF_6 is a low-melting very volatile solid (MP 64^0C; vapor pressure 115mm/25^0C) and is almost as reactive/corrosive as is elemental fluorine which readily reacts with metals, glass, plastics and ceramics. To handle this compound a wide range of materials that do not react with UF_6 needed to be developed. These included relatively low molecular weight liquids for coolants, higher molecular weight materials for lubricants, and polymers that could be fabricated into coatings, gaskets, valves and tubing.

In the 1930's industrial research with fluorocarbons was in its infancy with Freon$^®$ compounds (chlorofluoro methanes and ethanes) being targeted to replace flammable, corrosive or toxic refrigerants (hydrocarbons, ammonia, sulfur dioxide) as a first application [3]. The Freon$^®$ compounds were prepared by reaction of chlorocarbons (CCl_4 and C_2Cl_6) with hydrofluoric acid. This chemistry would not work for compounds of three or more carbon atoms as the corresponding perchlorocarbon precursors are unstable. Academic research efforts directed at preparations of higher molecular weight fluorocarbons by reacting liquid hydrocarbons with elemental fluorine found the main product to be CF_4 with a low yield of a broad distribution of higher molecular weight fluorocarbons. Separating individual fluorocarbons from such complex mixtures was difficult and impractical on a large scale as was the use of elemental fluorine.

In 1940 the possibility of using higher MW fluorocarbons as an inert material for direct contact with UF_6 was suggested by Joseph Simons of Pennsylvania State College who later provided a 2 ml sample of liquid fluorocarbon for testing [4]. This material displayed desirable properties to be used in direct contact with UF_6, and classified work directed by US Office of Scientific Research and Development began development of fluorocarbon materials for UF_6 handling applications. Later as part of the Manhattan Project, this effort to seek practical methods for preparation of large quantities of liquid and solid fluorocarbon materials brought together several academic and industrial research organizations in an accelerated effort to develop and produce various fluorocarbon materials in quantities over 1000 Kg needed for the $^{235}UF_6$ processing equipment [2]. A key problem was to avoid or minimize the use of elemental fluorine as a reagent because its production and use entailed low yields, difficult product separations and explosive hazards.

The use of hydrofluoric acid as the fluorine source reagent provided alternate and successful routes to fluorocarbons for which pilot plants were rapidly established [5]. One route involved chlorination of alkanes followed by catalyzed fluorine-chlorine exchange using HF to produce gases and liquids up to chain lengths of eight carbons [5a]. Another route developed an improved method for preparation of tetrafluoroethylene monomer [5b] which helped to scale up the production of poly(tetrafluoroethylene). This polymer, which was earlier discovered (1938), patented (1941) and later marketed as Teflon$^®$ by DuPont, found use in UF_6 operations as

gaskets, valve packings and insulation. Its technology also was the basis of fluorotelomer surfactants developed by DuPont 20 years later. Poly(tetrafluoroethylene) could not be melt- or solution-processed which limited its fabrication for many UF_6 processing needs. A route to a closely related polymer, poly(chlorotrifluoroethylene), was discovered, and this polymer had the requisite inertness and processability needed in UF_6 operational equipment [5c]. This polymer underwent accelerated pilot plant production [5d] and was later commercialized as Kel-F™ by M W Kellogg Company and acquired by 3M Company in 1957 [6]. Finally, early during the Manhattan Project an electrochemical fluorination process for direct substitution of fluorine for hydrogen in organic compounds conducted in a single-cell compartment using hydrofluoric acid as the electrolyte-supporting medium and fluorine source was invented by J. H. Simons [7, 8]. For security reasons this work was withheld from publication until after WWII when several patents [9] and publications [4, 7, 8] appeared. In 1946 these patents were assigned to 3M Company who continued after the end of the Manhattan Project to fund Prof. Simons' fluorocarbon chemistry research at universities through the 1950's.

The Simons cell electrochemical fluorination process and products were rapidly developed by 3M Company with a pilot plant in operation in 1947 and a commercial production plant in 1951 [10]. The unique properties that the new fluorocarbons possessed (exceptional chemical, thermal and radiation stability, exceptionally low surface energy, viscosity, refractive index and dielectric constant; and combined hydrophobicity and oleophobicity) enabled 3M to market a broad array of new products (refrigerants, propellants, heat transfer fluids, gaseous dielectrics, fire extinguishing agents, lubricants, surfactants, treatments for water and stain resistance in textiles, leather and paper; and polymeric plastics, rubbers and coatings) in the 1950's decade [6, 11]. Of particular importance for surfactant development was the single step conversion of octanoic acid and octylsulfonic acid to the acid fluorides of PFOA and PFOS [6, 12, 13]. PFOA and PFOS were not particularly useful surfactants themselves, but their acid fluorides were very important intermediates in the preparation of families of perfluoroheptylamide and perfluoroheptylsulfamide surfactants which exhibit remarkable properties in dilute aqueous solution for surface tension lowering and foam formation [6, 13]. Betaine example structures with amide and sulfamide linkages of are depicted below [6].
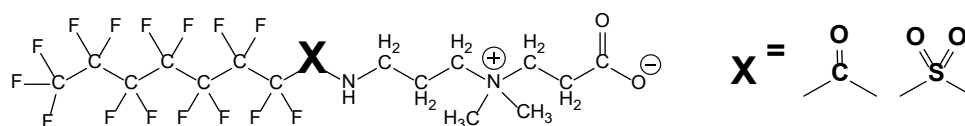
These categories of surfactants became the critical component in the discovery of their use in firefighting foam formulations at NRL [14, 15]. From 1960 to 1964 surfactants contributed by 3M were evaluated in foam formulations and compared with protein-based foams for extinguishing fuel fires. The fire suppression performance of the fluorosurfactant based formulations was superior to, and the extinction mechanism was significantly different from that of the protein based firefighting foams. To differentiate fluorosurfactant foams having these unique properties from other foams, the term "Light Water" was applied to them [14, 15]. Foam generation and dispersion hardware were developed, and a specification for "Light Water" foam formulation concentrates to be used by the military was issued (MilSpec MIL-F-23905) in 1963 with subsequent revisions in the 1963-1967 timeframe. In 1966, "Light Water" was trademarked

by 3M for these surfactants [16], and in later years 3M and other manufacturers began commercialization of fluorosurfactant based firefighting foam formulations. In 1969 MilSpec F-24385 was issued superseding MilSpec MIL-F-23905 accompanied by changing the MilSpec foam composition description from: "*one type and grade of "Light Water" liquid concentrate fire extinguishing agent consisting of non-toxic fluorocarbon surfactants and appropriate foam stabilizers*"; to: "*aqueous film-forming foam (AFFF) liquid concentrate fire extinguishing agents consisting of fluorocarbon surfactants and other compounds.*" This "AFFF" designation reflected both the mechanism of fire suppression and the necessity of fluorosurfactants as understood at that time [14]. It is noteworthy that both MilSpec documents specified the use of gasoline as the fuel for fire suppression testing.

In the 1970's a second fluorosurfactant technology derived from the telomerization of tetrafluoroethylene was developed and commercialized by DuPont. This was based on the reaction of IF_5 with $CF_2=CF_2$ to produce isolated iodo-terminated tetrafluoroethylene telomers then reacted with ethylene to yield 2-perfluoroalkylethyl iodide intermediates followed by conversion of these iodides to a variety of surfactants via alcohol, thiol, surfuryl chloride or surfuryl cyanate intermediates [17]. The key structural feature is the $-CH_2-$ or $-CH_2CH_2-$ structural element in the surfactant tail connecting it to the surfactant head group making it a polyfluorosurfactant as opposed to a perfluorosurfactant. An example structure analogous to the perfluorosurfactant above is depicted below. In the 1980's fluorotelomer surfactants were incorporated into commercial AFFF formulations [18].
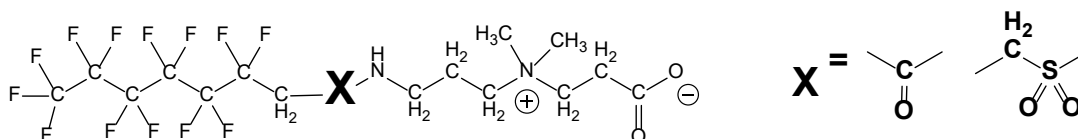
Toxicity of fluorocarbon organic compounds was a known issue in the 1940's but somewhat limited to ω-fluorocarbons [19] particularly fluoroacetates which were used as rodent poisons and insecticides [5e, 6]. With regard to fluorocarbon surfactants, the hydrophilic functional head groups that provide surface activity also provide environmental mobility and ingress to living organisms. The inert fluorocarbon surfactant tail makes these surfactants resistant to metabolism, excretion and biodegradation. Accumulation of organic fluorocarbon in human blood was reported in 1976 [20]. PFOA and PFOS bind to blood protein and accumulate in liver and gall bladder [21]. During the next two decades use of PFOA and PFOS derived surfactants expanded, and their disposal in the environment resulted in later widespread detection of their degradation products (PFOA and PFOS) in ground water [22] with a global distribution in wildlife [23]. From the 1990's improper disposal of fluorocarbon wastes became a serious health problem and legal problem including undisclosed PFOA and PFOS toxicity testing by 3M and DuPont as reported in a media narrative [24]. In 2000, following negotiations with EPA, 3M announced a voluntary phase out of PFOS chemical products. Enforceable consent agreements were negotiated with other fluorocarbon manufacturers regarding disclosure of production, toxicity testing and environmental monitoring in 2003. The EPA and eight major companies in the fluorocarbon industry launched the PFOA Stewardship Program in 2006. A key commitment of this program was to withdraw from production any fluorosurfactant with a perfluorocarbon

chain length greater than six carbon atoms by 2015. Replacing the fluorocarbon-surfactant component with a fluorine-free surfactant, while maintaining the high fire suppression performance, is an important and imperative research objective in view of more restrictive regulations from the EPA and likely discontinuation of fluorosurfactants' use in the future [25]. To date there are several fluorine-free firefighting foam concentrates commercially available, but none have a performance level sufficient for MilSpec qualification [26].

Gasoline vs Heptane. As indicated in the introductory paragraph, our research has detected a divergence in effectiveness of fluorine-free foam formulations to extinguish pool fires of heptane versus gasoline which is not observed when evaluating fluorosurfactant based AFFF formulations. The selection of heptane for initial small scale 19 cm diameter pool fire extinction testing was a logical approach as this fuel is readily available and invariant of composition unlike alcohol-free unleaded gasoline whose composition is dependent on source and season of purchase. With the exception of MilSpec, heptane is also the test fuel prescribed by most international standards (Table 1) [27].

Table 1. Fuel and Test Parameters for Fire-Fighting Foam Evaluation Designated by International Standards [27].

Standard[1]	Fuel Type	Pool Size (m^2)	Extinction Time (sec)	Application Density $(L^2/min \cdot m^2)$
MIL-F-24385F	Gasoline (unleaded)	2.6 4.65	≤30 ≤50	1.65 2.5
ICAO	JP5, Kerosene	2.8 4.5	≤60	4.1 2.8
IMO	Aliphatic HC (BP 84-105°C)	4.5	<300	2.5
ISO	Aliphatic HC (BP 84-105°C)	4.5	depends on class	2.5
LASTFIRE	Heptane	4.5	<420	3.2 or 2.5
UL	Heptane	4.65	<180	4

[1]ICAO: International Civil Aviation Organization; IMO: International Maritime Organization; ISO: International Organization for Standardization; LASTFIRE: Large Atmospheric Storage Tank Fires: UL Underwriters Laboratories

As will be described in the results section, a fluorine-free poly(oxyethylene)siloxane-alkylpolyglycoside formulation was developed to the point of approaching an AFFF formulation extinction time performance on the 19 cm diameter heptane pool. Advancing it to the 28 ft^2 pool MilSpec testing with gasoline fuel resulted in neither fire knockdown nor extinction. This unexpected result led to a review of the composition of gasoline vs heptane, the use of gasoline

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in a 19 cm pool fire extinction evaluation and a literature search for reports of gasoline vs heptane pool fire extinction testing. These first two items are presented in the results section and the third item is discussed in the next paragraphs.

The literature search located a series of publications by A. A. Briggs of the UK Fire Research Station over the years 1979-1996 reporting fire suppression testing with a variety of fuels which included gasoline, heptane, kerosene and a toluene-pentane mixture [28-34]. Foams included those based on protein, fluoroprotein and AFFF formulations. A sample of relevant control time and extinction time data is given in Table 2 [32]. These data were interpreted that the gasoline pool fire is the more difficult to control/extinguish and that the aromatic components in gasoline are the cause. Briggs went on to conclude, "…heptane is undesirable as a general-purpose test fuel insofar as it shows no differences of behavior where they are known to exist in commonplace incidents. Heptane fires were extinguished by a simple protein foam." [32] It is noted that Briggs' extinction times do not meet the MilSpec qualification of ≤50 sec indicated in Table 1 and that Briggs does not identify the AFFF or fluoroprotein foam concentrates by either tradename or composition. Nevertheless, the performance difference in fire suppression between gasoline and heptane fuel fires is substantial.

Table 2. 4.5 m^2(50 ft^2) Pool Fire Suppression Testing of Fluoroprotein and AFFF foams on Various Fuel Fires (data from ref [32] Foams C and Q, Table 4)

Foam	Gasoline		Pentane/Toluene(40%)		Heptane	
	Control	Extn	Control	Extn	Control	Extn
Fluoroprotein	36	144	90	215	27	81
AFFF	28	360	60	300	25	57

Control: time (sec) for 90% extinction

More recently (2013) MilSpec testing of commercial AFFF formulations has been conducted comparing gasoline and heptane fire extinction on both 28 and 50 ft^2 pools [35]. The gasoline vs heptane extinction time results for three commercial AFFF formulations from the MilSpec qualified products list are presented in graphic form in Figure 1. The extinction time results were within that required for MilSpec qualification as indicated by the dashed horizontal lines. The differences in extinction times on the 28 ft^2 pool for gasoline and heptane are relatively small. On the 50 ft^2 pool, the variation is larger (10-14 sec differences) in two cases and nominal in a third case. Overall, these data support assertion that extinction time differences for gasoline and heptane fuels is nominal for fluorosurfactant based AFFF formulations.

With respect to development of fluorine-free foam (F3) formulations there is little recent data comparing gasoline vs heptane fire suppression performance. Our initial observation of a large difference when progressing from benchtop/heptane testing to 28 ft^2 MilSpec/gasoline testing in the development of a poly(oxyethylene)siloxane-alkylpolyglycoside F3 formulation indicated the fuel identity to be a critical variable. This fuel identity variable should be investigated for currently available commercial F3 formulations as well. In cases where a fuel based divergence in suppression effectiveness is observed, experiments are undertaken to identify responsible gasoline components. By initially conducting testing and gasoline component effects at a benchtop scale, testing progressed more rapidly with examination of a breadth of variables (foam
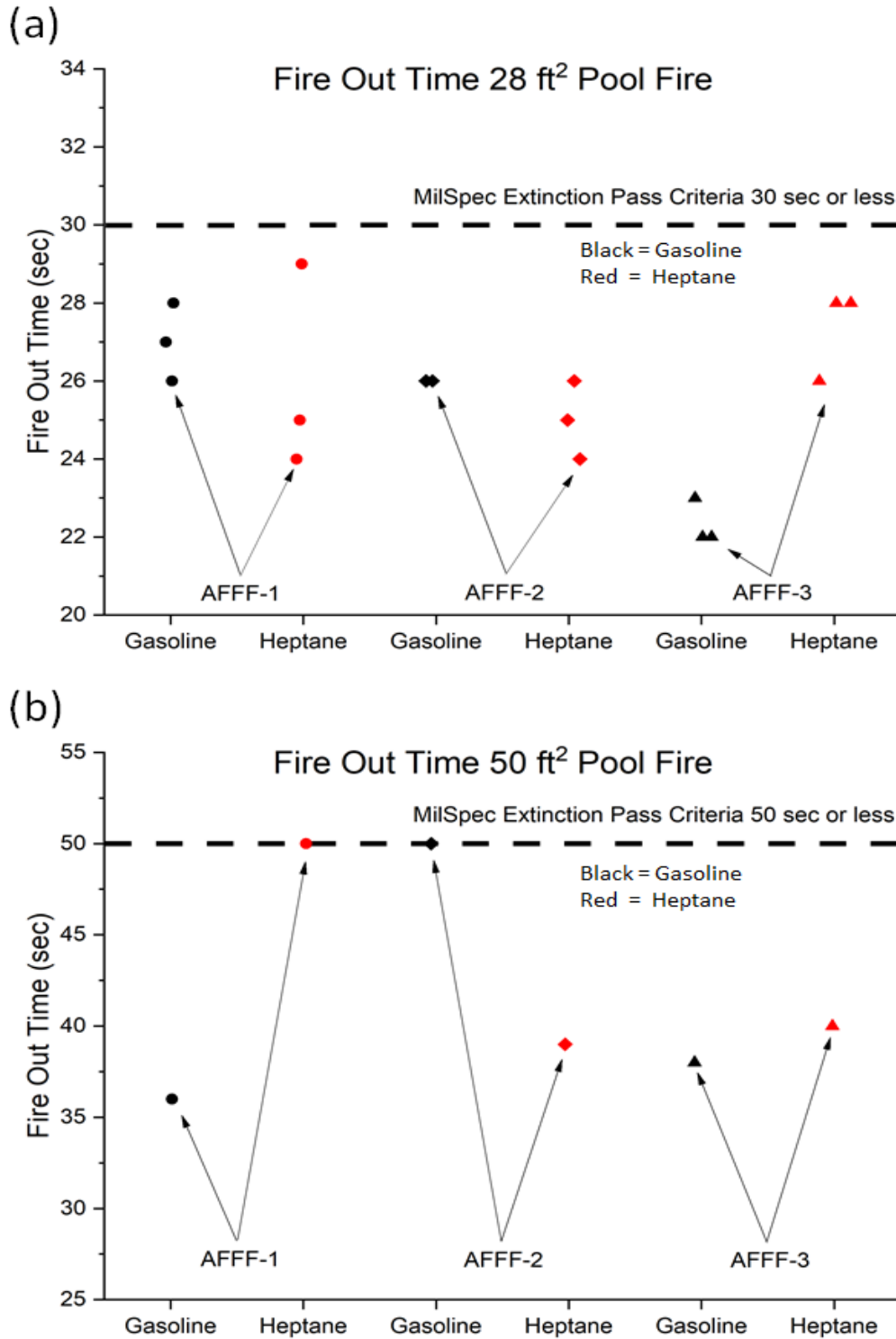
Figure 1. Comparative gasoline vs heptane fire extinction times for commercial AFFF formulations AFFF-1, AFFF-2 and AFFF-3: (a) 28 ft² pool and (b) 50 ft² pool. Data are from reference [35].

application rate, surfactant/formulation concentration, isolated gasoline components and their concentrations) at a significantly lower cost. This memorandum report documents results of our 19 cm diameter pool extinction testing examining these variables on both our experimental F3 and commercial F3 formulations.

MilSpec Revision. A pending revision of the current MilSpec, MIL-PRF-24385F is anticipated to issue in the near future as Mil-F-24385G. A major change anticipated is that the current unleaded, alcohol-free gasoline fuel will be replaced by commercial grade heptane for the 28 and 50 ft^2 pool fires along with a qualification extinction time increase of 5 seconds (30 to 35sec/28 ft^2 pool; 50 to 55sec/50 ft^2 pool) [36]. With respect to this future fuel change and to the anticipation of new F3 formulations emerging from research for MilSpec qualification, the new MilSpec draft comments in its Section 6 Notes are as follows [36]:

> *6.1 Intended use. The concentrate is intended for use in mechanical foam generating equipment such as fire-fighting trucks or foam sprinkler systems for extinguishing fires in flammable and combustible liquids such as gasoline or fuel oils. The foam generated is capable of extinguishing flammable and combustible liquid fires more quickly than non-Milspec foam, which is especially important where personnel and ordnance are in close proximity to the fire.*

> *6.6 PFOA and PFOS content. The DoD's goal is to acquire and use a non-fluorinated AFFF formulation or equivalent fire-fighting agent to meet the performance requirements for DoD critical fire-fighting needs. The DoD is funding research to this end, but a viable solution may not be found for several years. In the short term, the DoD intends to acquire and use AFFF with the lowest demonstrable concentrations of two particular per- and polyfluoroalkyl substances (PFAS); specifically PFOS and PFOA. The DoD intends to be open and transparent with Congress, the Environmental Protection Agency (EPA), state regulators, and the public at large regarding DoD efforts to address these matters. AFFF manufacturers and vendors are encouraged to determine the levels of PFOS, PFOA, and other PFAS in their products and work to drive these levels toward zero while still meeting all other military specification requirements.*

The first note indicates an intent to address gasoline fires with qualified concentrates, and the second note indicates a DoD goal to acquire and use F3 formulations for firefighting needs but with an expectation that it may be several years before qualified F3 formulations emerge from research. In the research summarized in this memorandum report, we hope to provide useful information for making progress toward the goals referred to in these notes.

Objective. The objective of this report is to provide comparative data, results and insights for two types of firefighting foam formulations: those that incorporate fluorocarbon surfactants referred to as aqueous film forming foam (AFFF) formulations and those that contain no fluorocarbon surfactants referred to as fluorine free foam (F3) formulations. The focus is on the hydrocarbon pool fire suppression effectiveness of the AFFF and F3 formulations and, in particular, on a divergence in extinction effectiveness of the F3 formulations when the pool fire fuel is heptane vs gasoline. In this report heptane is a commercial heptane composed of mixed isomers and not the pure *n*-heptane isomer unless explicitly referred to as such. Gasoline is the

alcohol-free unleaded gasoline currently used for MilSpec evaluations of AFFF formulations and is a complex and variable mixture of alkanes, cycloalkanes, alkenes and aromatic components. The composition of these fuels, particularly the gasoline, is an important determinant of the F3 formulations' level of effectiveness in fire suppression. Experiments are conducted to identify specific components of the gasoline that strongly degrade F3 formulation fire suppression capability and identify a mechanism by which this is thought to occur. While this research is continuing, the intent of this report is that this information be circulated for consideration in the MilSpec revision process.

EXPERIMENTAL DETAILS

The sources of experimental information and data in this report are NRL Notebooks N-10358 and N-10477.

Materials

Solvents, fuels, reference compounds, surfactants, AFFF and F3 concentrates were obtained from a variety of sources as identified below and used as received.

Solvents. n-pentane 99% (Aldrich 15,495); *n*-octane 99% (Phillips 66); *n*-nonane 99% (Alfa Aesar A16177); *n*-decane 99% (Phillips 66); *iso*-octane 98% (Fisher O301-4); methylcyclopentane 95% (Acros Organics 345245000); methylcyclohexane 99% (Acros Organics 126580010); 1-hexene 98% (Alfa Aesar B20271); benzene 99.8% (Aldrich 270709); toluene (Fisher T324-1); xylenes (Fisher X-5); *1,2,4*-trimethylbenzene 98% (Acros Organics 140090010); Butyl Carbitol®, diethyleneglycol monobutylether, DGBE, 99% (Aldrich 579963).

Solvents for NMR. Deuterium oxide-d2 99.9%D (Cambridge Isotope: DLM-4-100); Chloroform-d 99.8%D (Aldrich 151823).

Fuels. Commercial Grade Heptane; alcohol-free unleaded gasoline (Tilley Oil and Gas Company).

Surfactants. Capstone™ 1157 Fire Fighting Foam Surfactant (Chemours, see [37, 38] and references therein for additional characterization); Glucopon® 215 UP and Glucopon® 225 DK (BASF Corp., alkylpolyglycoside see [37, 38] for additional characterization; 502W Additive (Dow Corning Corp).

AFFF Concentrates. Reference AFFF (Ref AFFF) formulation concentrate was prepared at a 3% proportioning rate by mixing by weight: 2 parts Glucopon® 215 UP, 3 parts Capstone™ 1157, 5 parts DGBE and 20 parts deionized water [37, 38]. Commercial AFFF concentrates include four products submitted by different manufacturers for MilSpec MIL-F-24385F evaluation and passed the pool fire extinction requirements. The identities of these products cannot be disclosed in this report and are referred to as AFFF-1 through AFFF-4 when their data are presented.

F3 Concentrates. The experimental 502W - Glucopon 225 DK - DGBE F3 is prepared as a wt/vol percent premix solution by dissolution of 0.200% 502W, 0.300% Glucopon 225 DK and 0.500% DGBE in deionized water. Commercial F3 concentrates include: National Foam Universal Green 3-3% Alcohol Resistant Synthetic Foam Concentrate (National Foam);

Table 3. SDS Composition Information for Commercial F3 Formulations.

Chemguard Ecoguard 3%F3

Section 2. COMPOSITION / INFORMATION ON HAZARDOUS INGREDIENTS

Common Name	CAS No.	Composition
proprietary hydrocarbon surfactants	confidential	10–40%
polysaccharide gum	confidential	0–2%
propylene glycol t-butyl ether	57018-52-7	1–2%
water	7732-18-5	<50%

Does not contain PFOS or derivatives thereof.

Fomtec Enviro 3x6

SECTION 3. Composition / information on ingredients

Substance	CAS Number	Contents
Diethylene glycol monobutyl ether	112-34-5	5–9%
Alcohols, C12-14, ethoxylated, sulfates, sodium salts	68891-38-3	1–2.9%
Sulfuric acid, mono-C12-14-alkyl esters, compds with triethanolamine	90583-18-9	5–9%
Amines, C12-14 (even numbered) –alkyldimethyl(N-oxides)	308062-28-4	0.1–0.9%

National Foam Universal Green 3-3%

3. COMPOSITION/INFORMATION ON INGREDIENTS (This product is a mixture.)

Component	CAS Number	Concentration*
Propylene Glycol Monobutyl Ether	5131-66-8	3 – 7%
Sodium Decyl Sulfate	142-87-0	1 – 5%
Sodium Octyl Sulfate	142-31-4	1 – 5%
Sodium Laureth Sulfate	68891-38-3	1 – 5%
Butanedioic acid, 2-sulfo-, C-isodecyl ester, disodium salt	37294-49-8	0.5 – 1.5%
1-Dodecanol	112-53-8	0.1 – 1.0%
1-Tetradecanol	112-72-1	0.1 – 1.0%

*Exact concentration withheld as trade secret.

Solberg Re-Healing Foam RF3%

3. Composition/information on ingredients

Ingredient	CAS Number	Concentration (%)
2-(2-butoxyethoxy)ethanol	112-34-5	<20
starch	9005-25-8	>1
Tris(2-hydroxyethyl)ammonium dodecylsulfate	119-96-8	<20
α-sulfo-ω-hydroxyl-poly(oxy-1,2-ethanediyl)C9-12 alkyl ethers, sodium salts	96130-61-9	<5
1-propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-, N-coco acyl derivs., hydroxides	61789-40-0	<20
1-propanaminium, N-(3-aminopropyl)-2-hydroxyl-N,N-dimethyl-3-sulfo-, N-coco acyl derivs., hydroxides	68139-30-0	<2.5
D-glucopyranose, oligomers, dodecyl octyl glycosides	68515-73-1	<5
sucrose	57-50-1	>1

Chemguard Ecoguard 3%F3 (Chemguard Ltd.); Fomtec Enviro ARC 3x6 (Dafo Fomtec AB); Solberg Re-Healing Foam RF3% (Solberg Scandinavian AS). Composition information from safety data sheets is given in Table 3.

Characterization and Properties

Non-Volatiles Content. Quantities of non-volatiles in the AFFF and F3 concentrates were measured by subjecting a small quantity of the liquid to sequential periods of increased vacuum at a rate such that foam formation and expansion beyond confines of the container does not occur. The general procedure is as follows. An analytical quantity of 600 mg concentrate is weighed into a 3 ml open top vial. The vial is placed in a 25 ml beaker, covered with a small watch glass to function as a foam expansion deflector if needed, and the vial-beaker-watch glass assembly is placed into a vacuum desiccator. The desiccator is very gradually evacuated while monitoring the liquid concentrates for bubble and foam formation until a pressure of 20 mm is attained without foam expansion filling more than half the 3 ml containing vial. This 20 mm vacuum is maintained for a 12 hr period after which the residual quantity of concentrate is weighed and the percent remaining solids calculated. This treatment is followed by a second 20 mm vacuum/12 hr treatment. The vacuum during subsequent 12 hr periods is progressively reduced from 20 mm to 12 mm to 7 mm to 2 mm and finally to a rotary pump maximum vacuum of ≤1mm for four 12 hr periods. The loss of volatiles is followed by residual mass measurements at the end of each 12 hr period. A bar graph plot depicts a volatiles profile characteristic of a particular concentrate. The non-volatiles profile for the AFFF and F3 concentrates are presented as Figures A1 and A2 respectively in Appendix A.

NMR Spectroscopy. The concentrates and their non-volatiles were characterized by NMR spectroscopy as a way of detecting any fluorine or silicon and as a ^{1}H NMR "fingerprint." The ^{1}H NMR spectral fingerprint of the non-volatiles was further analyzed by spectra of methanol-soluble and methanol-insoluble fractions. The ^{1}H, ^{19}F and [29]Si spectra were recorded using a Bruker Advance 300MHz NMR spectrometer equipped with a standard BBO 300MHz S1 5mm probe and operating at 282.38 MHz with a 11.50 µsec 90° power pulse. Solutions for spectra of the commercial concentrates were prepared by dissolution of 60-70 mg of concentrate in 650-700 mg D_2O. Likewise, solutions for spectra of the non-volatiles portion of concentrate were prepared by dissolution of 20-30 mg of residue from the non-volatiles determination in 650-700 mg D_2O. Samples for the methanol-soluble and methanol-insoluble were prepared by addition of 600-620 mg of concentrate to 6.0-6.2 g of methanol, stirred 24 hr in 10 ml centrifuge tube, centrifuged, clear methanol solution decanted into vial, methanol-insoluble precipitate was washed with 2-3 ml methanol, recentrifuged and methanol wash discarded. The methanol solution was evaporated overnight, then the methanol-soluble and methanol-insoluble were dried by slow application of vacuum down to <1mm for 3 hr. ^{1}H NMR spectra of the methanol-soluble and methanol-insoluble fractions were recorded from D_2O solutions of these fractions. The methanol-insoluble solution in D_2O was often quite viscous at 25mg/650g D_2O, and its concentration was reduced to 3mg/700mg D_2O. These NMR spectra are presented in Appendix B.

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Surface/Interfacial Tension Measurement. Static surface tension was measured on concentrates diluted with deionized water to the premix solution concentration (3% of concentrate) using a ring (radius 9.58 mm, wire radius 0.185 mm) tensiometer at 20°C (Du Nouy Model Sigma 701, Biolin Scientific Inc., Gothenburg, Sweden). Interfacial tensions were measured with the ring tensiometer between the premix solutions and two fuels (heptane and gasoline) at 20°C.

Pool Fire Extinction Evaluation

Pool fire extinction tests were conducted using concentrates diluted to premix concentrations at benchtop and MilSpec field test scales.

Concentrate Premix Solution Preparation. The experimental siloxane-glycoside formulation premix solution was prepared directly from its components by dissolution of 8.0 g 502W, 12.0 g Glucopon 225 DK and 20.0 g DGBE in 4.000 L deionized water. Note: this formulation containing the 502W siloxane surfactant is prepared immediately before testing to exclude any slow siloxane hydrolysis from affecting the extinction test result. The Ref AFFF formulation premix solution was prepared by dissolution of 12.0 g Capstone 1157, 8.0 g Glucopon 215 UP and 20 g DGBE in 4.000 L deionized water. The commercial F3 concentrate premix solutions were prepared by dissolution of 120 ml of the concentrate in 4 L deionized water. The foregoing solution quantities were used for benchtop testing and were scaled up to a volume of 10 gal per 28 ft^2 MilSpec test.

Benchtop Extinction Testing. Benchtop pool fire extinction tests were conducted in a 19 cm diameter glass crystalizing dish incorporated with an air sparging foam generating device into an apparatus described in ref [38]. Briefly, its operation involves filling the pool with water up to 2 cm from the top edge followed by a 1 cm thick layer of hydrocarbon fuel. The air flow through the foam generator is then fixed at a particular setting and a foam flow rate and foam expansion ratio are determined by measuring the time needed to fill a 500 ml beaker and the mass of the 500 ml of collected foam. Next the pool is ignited for a 60 sec preburn period and immediately after the foam is directed through a tube to the center of the burning pool. The times from start of foam deposition on the burning pool to foam coverage of the pool surface and to fire extinction are measured. The foam deposition is then redirected into an empty 500 ml beaker for a second determination of foam flow rate and foam expansion ratio. This test is repeated at different foam flow rates that can range from 100 to 2500 ml/min. The extinction profile (plot of foam flow rate vs extinction time) provides a useful metric for comparing extinction performance of foamed surfactants and their formulations.

MilSpec Extinction Testing. The MilSpec field test is a Department of Defense evaluation standard [39] for use of firefighting foam concentrate in military installations, ships and aircraft. Testing performed was limited to the 28 ft^2 pool fire extinction, burnback, 25% liquid drainage and expansion ratio measurements. The extinction test is conducted by adding 10 gal of alcohol-free unleaded gasoline to a 4 in high, 6 ft diameter cylindrical steel pan with a water under-layer, igniting within 30 sec after gasoline addition, allowing a 10 sec pre-burn time, and extinguishing by manual foam application at a 2 gal/min rate through a nozzle with an inlet pressure of 100 psi. The extinction time is measured between the start of foam deposition on the pool fire and extinguishment. The foam deposition continues for a total of 90 sec after which the burnback

test is conducted. The burnback test is conducted 60 sec after completion of foam deposition and involves re-ignition of the pool fire by the lowering of a small pan (2 in high, 1 ft diameter) containing 1 gal of ignited gasoline into the center of the pool and removing after fire spreads outside of the pan. The burnback time is measured from the time of contact of the pan with the fire until the fire has spread to cover 25% of the foam-covered pool. The expansion ratio is measured by collection of a measured volume of foam (500 ml from benchtop apparatus or 1000 ml from MilSpec field test apparatus) and weighing this foam quantity to determine the corresponding volume of liquid. The 25% foam drainage measurement is conducted by collecting the foam in a 500 ml graduated cylinder and measuring the volume of liquid drained as a function of time.

EXPERIMENTAL RESULTS

The results described in this section include a recounting of an experience in a side-by-side transitioning of benchtop to MilSpec field testing for an experimental fluorine-free foam formulation and a fluorosurfactant based Reference AFFF formulation. Both formulations tested positively at the benchtop evaluation but totally diverged at the MilSpec testing. Analysis for the cause of this large divergence in testing was found to reside in the different fuels used: heptane for benchtop testing and gasoline for MilSpec testing. This observation involved a fluorine-free siloxane-glycoside foam formulation and brought into question whether other fluorine-free foam formulations, particularly commercial ones, would also display this divergent behavior in gasoline vs heptane fire suppression testing. Several commercial F3 formulations were purchased and benchtop fuel comparative testing was conducted. These results are reported in the second section. The underlying cause for the gasoline vs heptane divergent F3 extinction behavior was investigated and these findings are reported in the third section. Finally, an evaluation and a proposal are made for a two component trimethylbenzene-heptane fuel to simulate gasoline is presented in the fourth section.

Development and Testing of an Experimental F3 and a RefAFFF Formulation

To mimic large scale MilSpec pool fire extinction testing on a small scale with a discriminating capability of firefighting foam formulation effectiveness, it is necessary to have a MilSpec qualifying reference formulation to use as a standard. While commercial MilSpec-qualified AFFF formulations are available, they are of complex composition, proprietary and subject to change. As an early development in our research, a simple three component formulation was devised consisting of two surfactants, a C6C2-fluoroalkyl sulfobetaine (Capstone™ 1157) and an alkyl polyglycoside (Glucopon® 215 UP) and an organic solvent (Butyl Carbitol®, DGBE) dissolved in water [37, 38]. The chemical structures are depicted in Figure 2 and have been characterized in the literature ([38] and references therein). This RefAFFF formulation has passed the current MilSpec 28 ft^2 pool fire extinction requirement (<30 sec) with a 26 second extinction time [38]. A photograph of the 28 ft^2 pool is displayed in Figure 3.

This RefAFFF formulation also serves as a valuable research tool in that the roles of the individual components may be investigated. As such, a structure-property correlation approach provides important leads for design and selection of fluorine-free surfactants to replace

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fluorocarbon surfactants. Exploratory experiments need to be done on a small scale to be practical. For such investigations our research has made use of a 19 cm diameter pool fire with a small air-sparge foam-generating apparatus. The ability to vary foam delivery rates over a range of 100 to 2500 mL/min enables characterization of surfactants and formulations by an extinction time – foam flow rate profile. This series of extinction tests consumes 5 to 10 g of surfactant and 1.5 to 3 L of fuel as compared with a single 28 ft^2 pool fire extinction test consuming 100 g of surfactant concentrate and 10 gal of fuel. A photograph of this benchtop apparatus is also displayed in Figure 3.
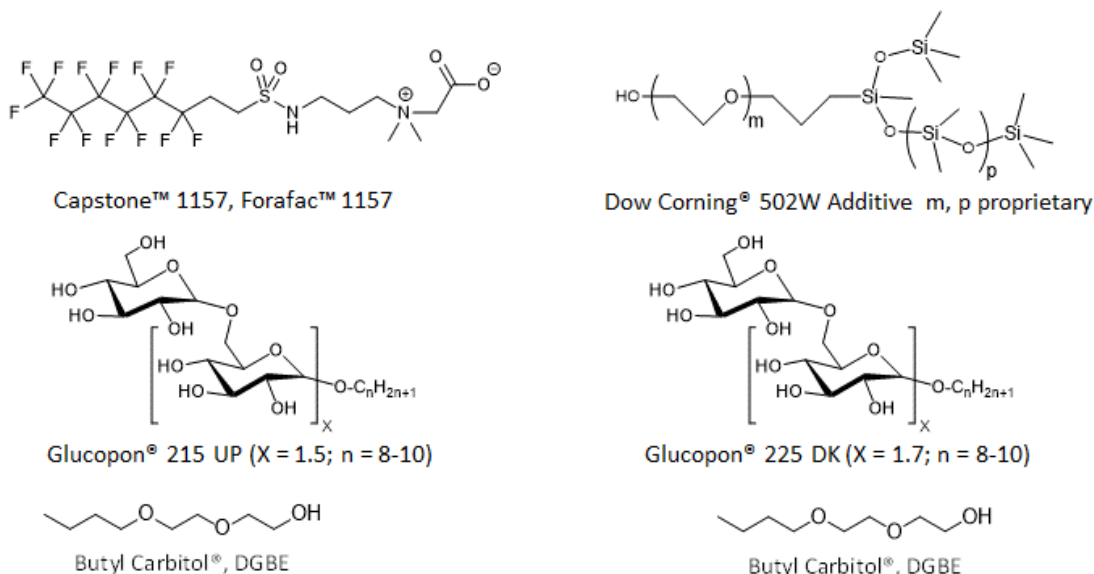
Figure 2. Chemical structures of components in RefAFFF and 502W-Glucopon 225 DK formulations.

Figure 3. Photographs of fire extinction testing apparatus: left - MilSpec 6 ft diameter, 28 ft^2 area pool; right – benchtop 19 cm (7.5 in), 284 cm^2 (43.9 in^2) area pool.

The use of the alkyl polyglycoside surfactant in combination with fluorocarbon surfactants in AFFF formulations originated from an important discovery in 1993 by Norman and Regina [40]. Its inclusion enabled a significant reduction in the quantity of expensive fluorocarbon surfactants in AFFF formulations while maintaining pool fire extinction performance with an overall cost reduction of 40-80% [40]. In current AFFF formulations additional functions of the hydrocarbon surfactant components are to maintain foam structure, and beyond this alkyl polyglycosides can increase the foam expansion ratio [18]. In the RefAFFF formulation of Figure 2, a 3:2 surfactant ratio of Capstone™ 1157 : Glucopon 215UP based on weight quantities of respective surfactant concentrates was the optimum for producing the shortest extinction time.

As a starting point, our approach toward replacing a fluorocarbon surfactant with a fluorine-free surfactant, the RefAFFF formulation was used, and substitution for the Capstone™ 1157 component with members of several series of commercial foam-forming hydrocarbon and siloxane surfactant candidates was investigated. Fluorocarbon surfactants have very unique oleophobic, hydrophobic and spreading properties along with exceptional thermal, chemical and foam stabilities making such a replacement exceptionally challenging. With one exception, foams generated from formulations based on these substitute surfactant candidates did not perform comparably to RefAFFF and in many cases fell short of pool fire extinction entirely. The one exception was the Dow Corning 502W Additive siloxane surfactant which, as the substitute in the RefAFFF formulation, displayed an extinction time – foam flow rate profile that was comparable to that of RefAFFF. By itself (without the alkyl polyglycoside co-surfactant) this surfactant is totally ineffective as is the alkyl polyglycoside surfactant when used by itself. The nature of this surfactant synergism is currently being studied.

The 19 cm diameter heptane pool fire extinction times as a function foam flow rate are plotted in Figure 4 for the RefAFFF and an evolution of siloxane-glycoside formulations. The RefAFFF extinction time – foam flow rate profile represents a performance goal which is derived from this formulation's passing the MilSpec pool fire extinction time requirement [38]. As indicated above, the screening of many commercial siloxane and hydrocarbon surfactants by substituting them for the Capstone 1157 surfactant in the RefAFFF formulation produced only one candidate that displayed an extinction profile remotely comparable to that of RefAFFF. The 502W substitution for Capstone at the 3:2 ratio with Glucopon® 215UP is plotted in Figure 4 (Siloxane #1). The surfactant ratio was then systematically varied from 3:1 to 1:3 with the finding that the best improvement occurred at the 2:3 ratio (Siloxane #2). Next, a series of four alkyl polyglycoside surfactants were tested with the finding that the 2:3 502W:Glucopon® 225DK (Siloxane #3) with its larger glycoside head group (Figure 2) closely approached the RefAFFF profile on the 19 cm heptane pool fire.

To further evaluate this Siloxane #3 formulation, a decision was made to conduct a MilSpec extinction test on the 28 ft^2 pool at NRL Chesapeake Bay Detachment (CBD). When this test was conducted, there was neither an extinction nor a fire knockdown. As a control experiment, the RefAFFF formulation was retested, and it again extinguished the pool fire in less than the 30 sec MilSpec requirement. Sources suspected for this divergent behavior included fuel identity (heptane vs ethanol-free gasoline), foam generation method (near ambient pressure bubbling

through a glass frit vs 100 psi passage through an aspirating nozzle), and pool size (correlation with heat intensity).
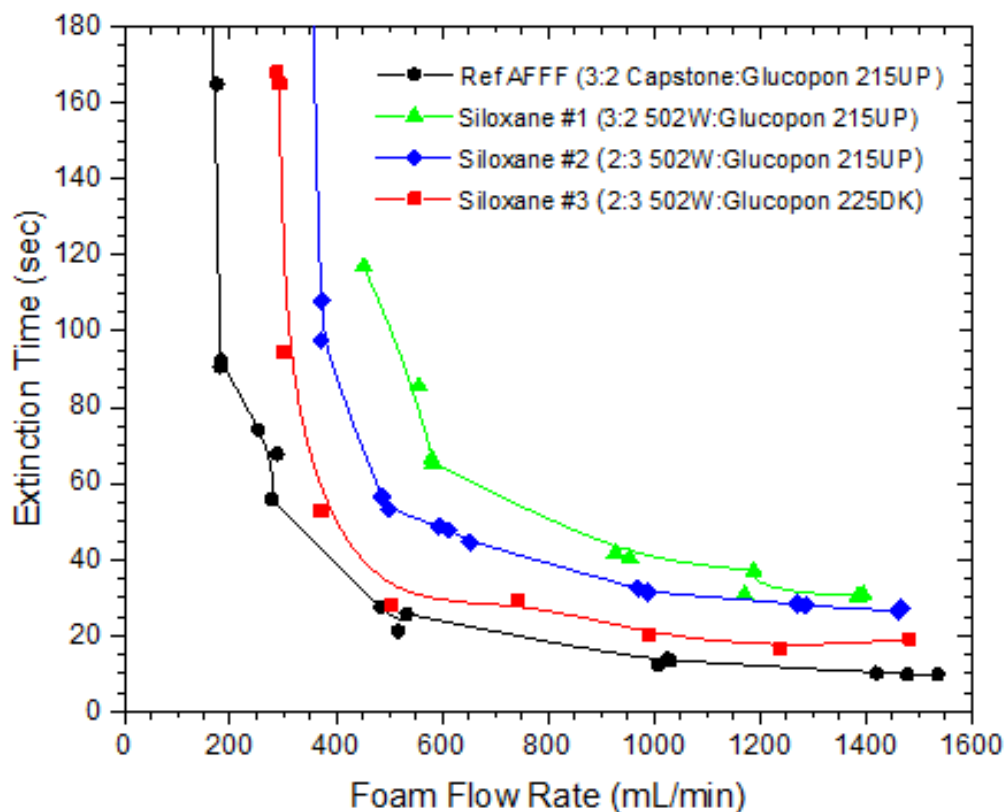

Figure 4. Profile of a 19 cm diameter heptane pool fire extinction time vs foam flow rate for the RefAFFF formulation and an evolution of siloxane-glycoside formulations based on 502W Additive siloxane surfactant and the alkyl polyglycoside surfactants Glucopon 215UP and Glucopon 225DK.

The alcohol-free gasoline used for the CBD MilSpec pool-fire testing was the first suspicious item to be investigated. It was used as the fuel in the 19 cm pool fire, and gasoline vs heptane comparative data were obtained (Figure 5). For the Ref AFFF the difference between extinction profiles is small with the gasoline pool-fire being slightly more difficult to suppress although both fuels could be extinguished in less than 20 sec at the 1200 mL/min foam flow rate. However, for the Siloxane #3 formulation the gasoline-heptane extinction profile difference is quite large with no extinction being observed at and below the 1200 mL/min foam flow rate. This remarkable difference is clearly attributable to the identity of the fuel and more particularly to the interaction of gasoline with components of the Siloxane #3 formulation.

For confirmation of this gasoline vs heptane effect on a larger scale, MilSpec testing on the 28 ft^2 pool fire was repeated with the Siloxane #3 formulation and the RefAFFF using heptane as the fuel to compare bench-scale and large-scale performance. At a flow rate of 2 gpm, the RefAFFF extinguished the heptane pool fire in 30 seconds while the Siloxane #3 formulation extinguished
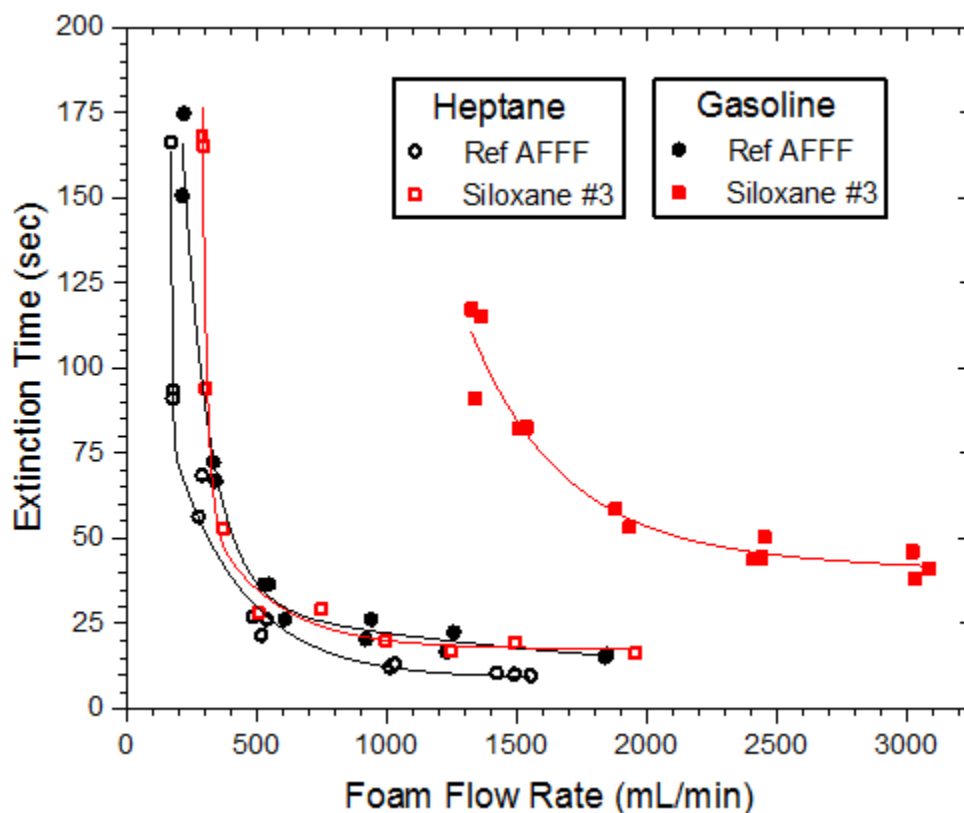
Figure 5. Comparative gasoline vs heptane pool-fire extinction profiles of RefAFFF and Siloxane #3 formulations on a 19 cm diameter pool.

the heptane pool fire in 51 seconds. This represents a substantial change in performance from the Siloxane #3 formulation being unable to extinguish a gasoline pool fire at large-scale, to extinguishing a heptane pool fire in 51 seconds. MilSpec data are presented in Table 4.

Table 4. MilSpec Results for 28 ft² Pool Fire Extinction, Burnback, Expansion Ratio and 25% Liquid Drainage Time for RefAFFF and Siloxane #3 Formulations

Test	MilSpec Criteria	RefAFFF		Siloxane #3	
Fuel	Gasoline	Gasoline	Heptane	Gasoline	Heptane
Extinction Time (sec)	≤ 30	24	30	No Extinction	51
Burnback Time (min)	≥ 6 (for gasoline)	12.39	16.35	No Extinction	5.63
Expansion Ratio	5-10	6.6	7.5	6.8	6.4
25% Liquid Drainage (min)	≥ 2.5 min	3.0	4.2	3.5	3.3

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Gasoline is a complex mixture of hydrocarbon components, and its composition varies depending on petroleum source, refining process and formulation for season of intended use. A simple ^{1}H NMR analysis was conducted on the gasoline used in the CBD testing and compared with the heptane fuel used in the benchtop testing and with *n*-heptane as well. Spectra of each fuel are presented in Figure 6. In the gasoline spectrum there are two groups of resonances: one in the 0.5-2.3 ppm range associated with protons bonded to aliphatic carbon structures and the other in the 6.8-7.2 ppm range associated with protons bonded to unsaturated carbon structures. Integration of these two groupings of resonances indicate that a significant quantity of aromatic and olefinic components reside in the gasoline. Within the aliphatic group, the resonances within the 2.0-2.3 ppm range correlate with methyl groups bonded to aromatic or olefinic structures. Examination of the heptane and *n*-heptane spectra provides further insight. Neither of these spectra display resonances corresponding to unsaturation in hydrocarbon structures. The heptane (or "heptanes" as commercial heptane is frequently termed) is a mixture of C7 alkane isomers and closely related cyclic hydrocarbons. The inset in the Figure 6 heptane spectrum is a typical composition of commercial heptane [41] and identifies the numbers of methyl, methylene and methine groups in each major component. The branched chain isomers accentuate the number of –CH$_3$ groups per molecule and result in an integration ratio of methyl to methylene/methine that approaches 1. In the single component *n*-heptane this ratio is 6:10 which is reasonably well approached by the experimental 1.00:1.58. The extra methyl groups in heptane do cause a small depression of its surface tension (19.8 mN/m at 19 ^{0}C) compared with that for *n*-heptane (20.0 mN/m at 19 ^{0}C) which can make a difference with respect to film formation on the fuel surface as calculated by spreading coefficient. With respect to gasoline, the non-aliphatic components appear to cause an increase in the surface tension (22.7 mN/m at 19 ^{0}C). However, as to be presented in a later section, the prevalent identified aromatic components in gasoline can cause a significant and negative effect in pool fire suppression by F3 formulations.

Two diagnostics that relate valuable information about foam-fuel interaction are a foam degradation test and a fuel-vapor transport test. Foam degradation was evaluated by monitoring the disappearance of a 4 cm thick layer of laboratory generated foam deposited over 60 ml of 35^{0}C heptane or gasoline in a 100 ml beaker (Figure 7). There is an increase in bubble size followed by a shrinking of the foam volume. A plot of foam height vs time depicts significant foam degradation differences between the heptane and gasoline fuels for the RefAFFF and Siloxane #3 formulations (Figure 8(a)). This plot indicates the stronger degrading character of the gasoline on the stability of the RefAFFF and siloxane #3 foams. Fuel vapor transport through a foam layer is measured by a similar but closed apparatus where the headspace air above the foam is transported through an FTIR gas cell and monitored for fuel vapor content. These data are plotted in Figure 8(b). This vapor permeation occurs on a shorter time scale than that of the foam degradation experiment. The results indicate that the Siloxane #3 foam is more susceptible to hydrocarbon vapor permeation and that gasoline is the more permeable vapor through both foams. It should be noted that these diagnostics are conducted under conditions significantly different from fire suppression.
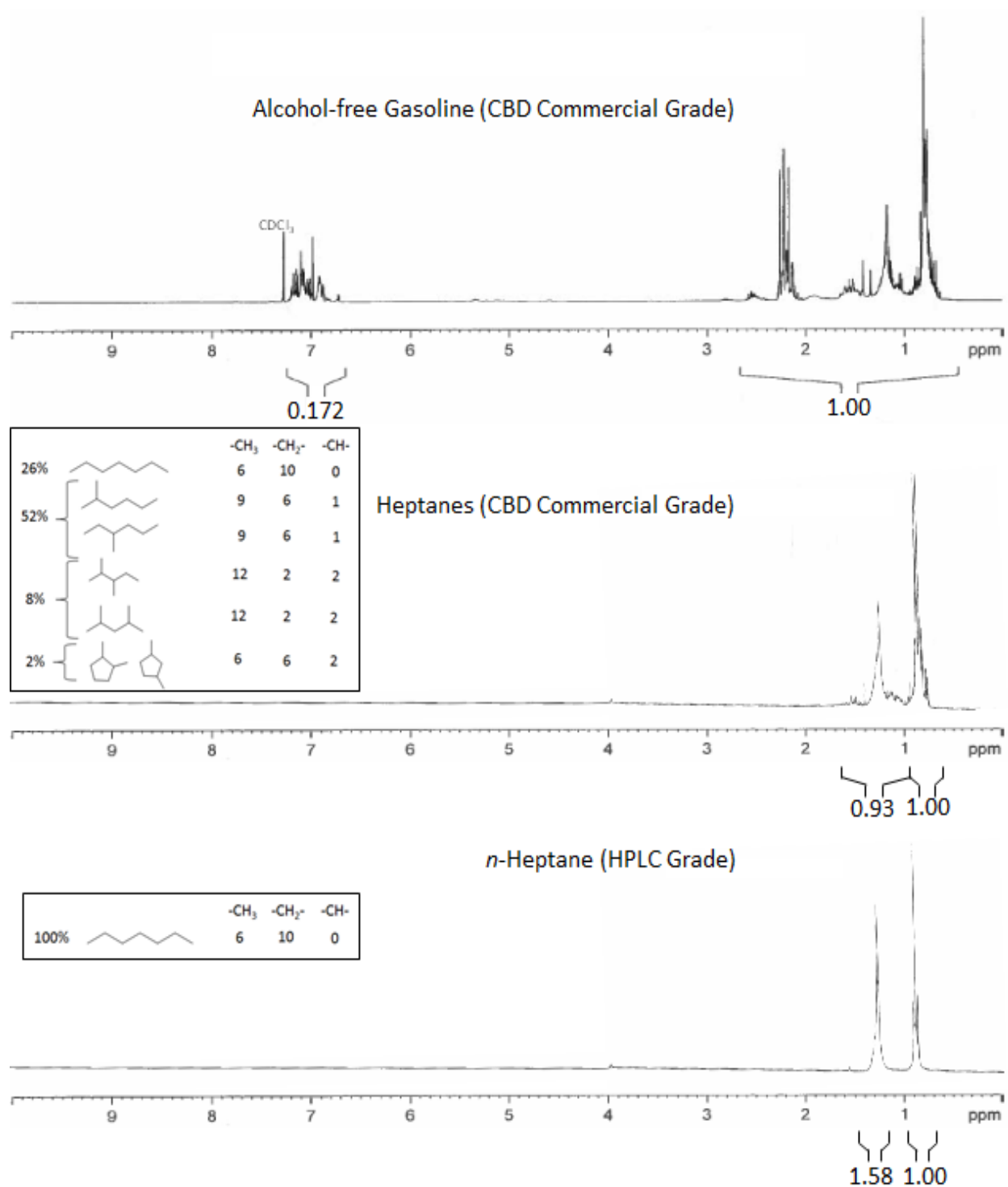
Figure 6. ^{1}H NMR spectra of alcohol-free gasoline, heptanes and *n*-heptane used in 28 ft^2 and benchtop pool-fire extinction testing. Integrations are discussed in the text. The inserts on the heptanes and *n*-heptane spectra identify quantities of major components [41] and the number of methyl, methylene and methane structural units in each component.
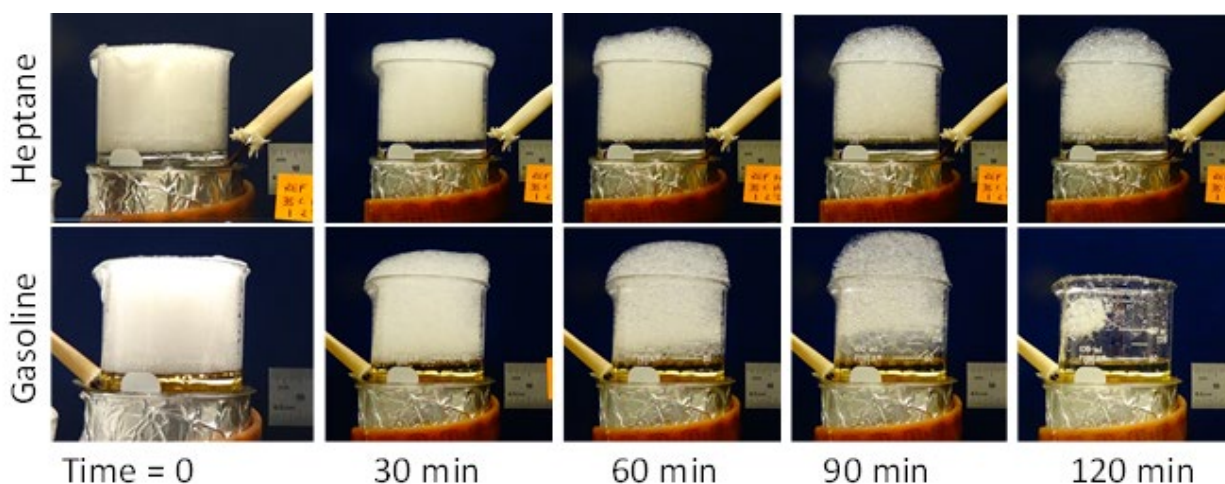
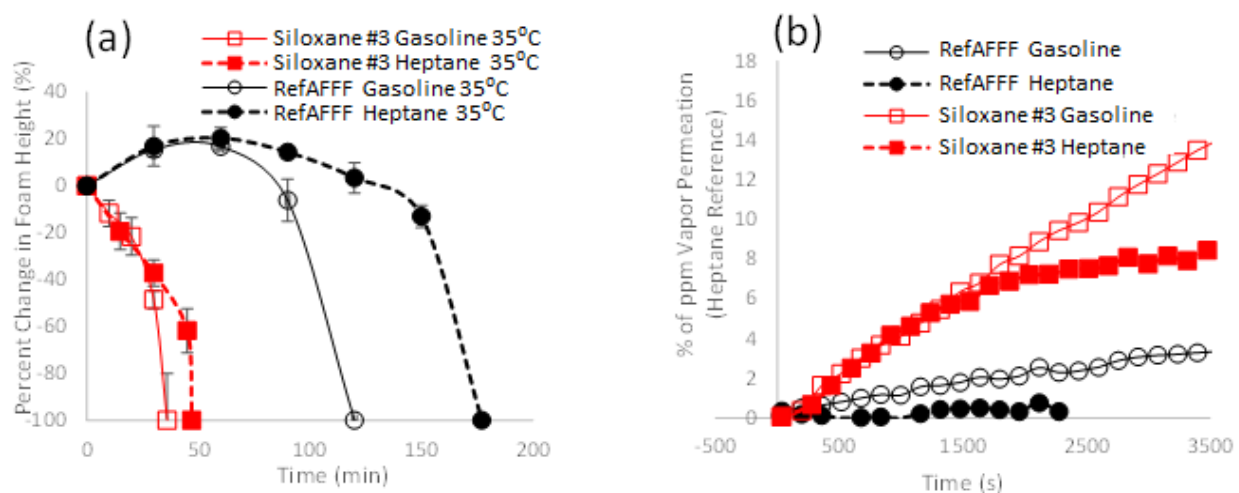Figure 7. Photographic images of RefAFFF foam degradation over heptane and gasoline at 35^0C.

Figure 8. (a) Plot of RefAFFF and siloxane #3 foam degradations over heptane and gasoline at 35^0C; (b) Plot of heptane and gasoline vapor concentration increase in the purged headspace following deposition of a 4 cm layer of foam over a pool of fuel.

Gasoline vs Heptane Fire Suppression Testing of Commercial AFFF and F3 Formulations

As described above and depicted in Figure 5, the use of gasoline or heptane as a pool fire fuel causes a large divergence in fire suppression behavior for an experimental F3 formulation based on a siloxane-glycoside surfactant formulation. This observation raises the question as to whether this may be a general characteristic of F3 formulations and whether there may even be a significant difference in AFFF extinction performance on pool fires of gasoline vs heptane. In

the introduction the cited literature references indicate that this issue is unresolved. In this section this issue is addressed for both AFFF and F3 formulations by conducting comparative extinction profile experiments with a benchtop 19 cm diameter pool fire apparatus under controlled conditions using gasoline and heptane as fuels.

Three AFFF formulation concentrates were evaluated, the first being the RefAFFF [38] described above and the second and third being commercial formulations, AFFF-3 and AFFF-4 respectively. These concentrates are characterized by non-volatiles component content determined by evaporation under stepped application of vacuum (Appendix A) and by fluorine content determined by ^{19}F NMR.[37] The RefAFFF concentrate has a non-volatiles content of 7.3 wt% and a fluorine content of 1.2 wt%. The AFFF-3 and AFFF-4 commercial concentrates have respective non-volatiles contents of 15 and 67 wt% and fluorine contents of 0.77 and 1.2 wt%. These concentrates were diluted at a proportionating rate of 3% and fire extinction profile data obtained using the standard procedure [38] and the benchtop apparatus depicted in Figure 3. The gasoline vs heptane pool fire extinction profile data are presented in Figure 9. The extinction time correlates with foam flow rates being rapid at rates >500 mL/min progressing to a non-extinction at rates <200 mL/min. The fire extinction dependence on the fuel identity is small. All three of these formulations extinguished the MilSpec 28 ft^2 gasoline pool fire in less than the required 30 sec.
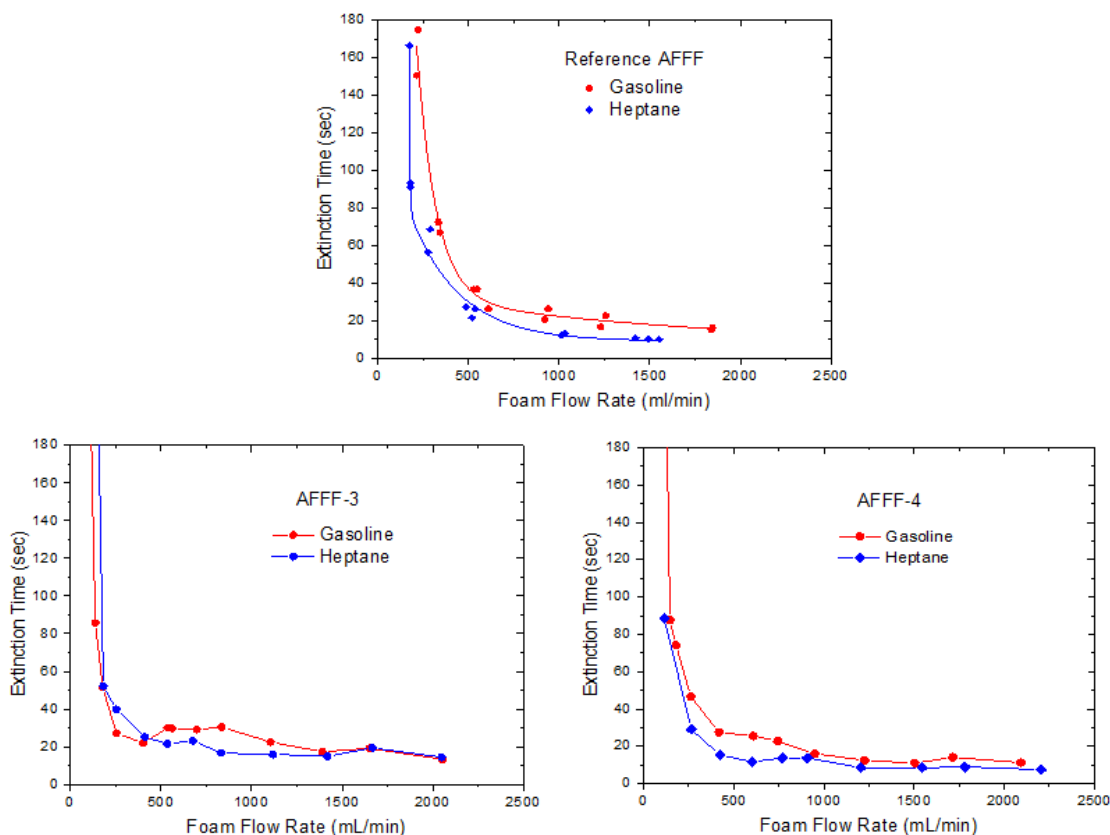

Figure 9. Comparative extinction time profiles of AFFF formulations for gasoline and heptane 19 cm pool fires.
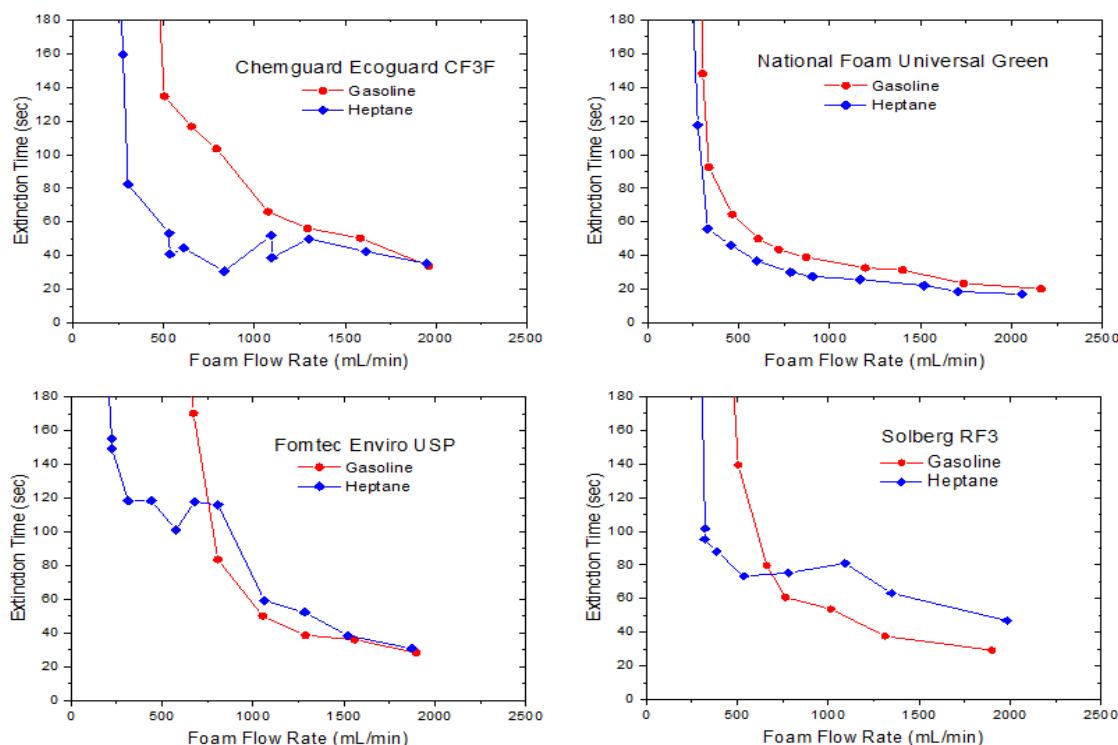
Figure 10. Comparative time extinction profiles of four commercial F3 formulations for gasoline and heptane 19 cm pool fires.

Commercial F3 formulations have been available for 10-20 years following toxicity and environmental issues raised [20-24] and action by the Environmental Protection Agency [42-44]. These F3 formulations are generally proprietary mixtures of fluorine-free surfactants and polymers in a somewhat viscous solution that generate wet foams with very slow drainage. General assessments of the fire-extinguishing performance range from optimistic [45] to pessimistic [46]. The issue of specific interest here is to determine whether the use of gasoline vs heptane as the pool fire fuel causes a significant difference in fire extinction when using commercial F3 formulations. Four commercial F3 formulation concentrates were evaluated. These were purchased from the manufacturer/distributor and include: Chemguard (Ecoguard 3%F3); Fomtec (Enviro ARC 3x6); National Foam (Universal Green 3-3%); and Solberg (Re-Healing Foam RF3). General composition information from SDS is presented in Table 3, but specific compositions are proprietary. The gasoline vs heptane pool fire extinction profile data are plotted in Figure 10.

The extinction profile results for these F3 products display considerable variation in effectiveness on both the gasoline and heptane pool fires and are considerably different from the profile of the Siloxane #3 experimental formulation presented in Figure 5. Unlike the AFFF formulations, none of the F3 formulations have an extinction time of less than 20 seconds at the high foam flow rate limit. The region of practical importance is the <1000 mL/min flow rate, and only the National Foam product shows an attractive performance within this region. With respect to the gasoline vs heptane issue, the extinction behavior is quite varied with two products displaying a crossover in effectiveness. In the <1000 mL/min flow region gasoline is the

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predominantly more difficult fuel fire to extinguish with the differences becoming quite large at the 500 mL/min flow rate.

While the intent here is not to analyze failures and limitations of the F3 formulations, there are some other properties of these formulations that are readily measured and have importance with respect to MilSpec requirements. These include non-volatiles and viscosity of the concentrate, surface and fuel-interface tensions of the premix and expansion ratio of the foam. These properties are reported for the AFFF and F3 formulations in Table 5. The variation in concentrate non-volatile component quantities and viscosity cover a substantial range. The AFFF formulations appear to reflect extremes with the three-component RefAFFF being composed of what is minimally necessary to generate foams and suppress pool fires without addressing other requirements and the AFFF-4 being heavily loaded with components for maximum versatility. The four commercial F3 formulations have variations in non-volatile content consistent with proprietary compositions, and the NRL experimental Siloxane #3 formulation has a relatively low non-volatiles content reflecting a minimal composition used to investigate extinction similar to that of the RefAFFF formulation. The viscosity of the concentrate is typically low for AFFF formulations and can be quite high for F3 formulations approaching that of a gel. Its importance is in compatibility with the equipment needed to rapidly dilute the concentrate (3 or 6%) to the premix concentration immediately prior to foam generation. In this regard MilSpec requires a concentrate viscosity range of 2-20 cP. High viscosity can enhance slow drainage of water from foam which many F3 formulations rely upon for fire extinction. Surface and fuel interface tensions of the AFFF and F3 formulations at their premix concentrations are important differences between these groups. The higher surface tension of the F3 solutions cause a negative spreading coefficient condition, and a continuous aqueous-surfactant film is not formed by drainage from a foam applied to the fuel surface. The lower surface tension AFFF solution drained from its foam can form a continuous film barrier and, along with the oleophobic character of the fluorinated surfactant foam above, can more effectively retard fuel vapor transport to the fire above the foam. Finally, the expansion ratio parameter should pass the MilSpec threshold of >5 such that the foam's dryness results in an efficient consumption of the concentrate. F3 formulations that utilize very wet foams (expansion ratio <5) and slow drainage can increase fire suppression effectiveness but at a high rate of consumption of the concentrate supply.

In addition to pool fire suppression, the AFFF and F3 formulations have differing concentrate, premix and foam properties and can be thought of as separate groups having related but different capabilities due to the uniqueness of the fluorocarbon surfactant in AFFF compared with the hydrocarbon surfactants in F3. These formulations have a different mechanisms for fire suppression, and improving on this capability results in the respective formulations developing different properties in their forms as a concentrate, a premix solution and a foam. These will be discussed in more detail in a later section. The main issue of interest is the divergent behavior of the F3 formulation in extinguishing of gasoline and heptane pool fires. Determination of what may be the underlying cause for divergence is undertaken in the following section.

Table 5. AFFF and F3 Concentrate, Premix and Foam Characterization.

F3 Manufacturer (Product)	Non-Volatiles Content (wt%)	Viscosity (cP)	Surface Tension (mN/N)	Gasoline Interfacial Tension (mN/N)	Heptane Interfacial Tension (mN/N)	Expansion Ratio
AFFF						
NRL (RefAFFF)	7.3	3.19	15.2	1.05	1.00	9.4
Manufacturer-3 AFFF-3	15.0	6.97	16.4	1.63	1.50	6.7
Manufacturer-4 AFFF-4)	67.4	9.84	14.1	2.74	3.36	6.0
F3						
Chemguard (Ecoguard 3%F3)	36.2	22	27.0	0.64	1.98	9.0
Fomtec (Enviro ARC 3x6)	21.2	150	24.0	1.00	2.74	6.5
National Foam (Universal Green 3-3%)	14.6	1700	23.1	3.61	5.11	4.4
Solberg (Re-Healing Foam RF3)-LV	30.1	30-60	26.1	0.56	2.40	7.7
NRL (Siloxane #3)	13.6	5.3	22.4	2.20	2.29	8.2

Gasoline vs Heptane Divergent F3 Extinction Behavior Analysis

A comparison of the extinction profiles in Figures 5, 9 and 10 shows that the Siloxane #3 formulation exhibits greatest divergence in gasoline vs heptane pool fires. For the heptane pool fire, its extinction profile approaches that of an AFFF formulation, while for the gasoline pool fire, its profile is far less effective than the other F3 formulations. The underlying cause for this divergence has been correlated with the content of gasoline having non-aliphatic components. To uncover a reason why F3 formulations exhibit this divergence in varying degrees, the Siloxane #3 formulation is examined for a deeper analysis of this phenomenon. In this section the isolated effects of these gasoline and surfactant formulation components will be examined to learn how these components interact, causing a degradation of extinction performance.

The composition of gasoline is variable depending on the season of the year and its source. Its content consists of over a hundred components, and analyses of gasoline composition is usually divided into various classes of compounds. The results of a recent analysis of four commercial gasolines is depicted in Table 6. The information in this table comes from Table 3 of ref [47] and is supplemented with specific compound content analysis from its supporting information. These individual compounds along with their content in each gasoline were selected as the predominant members of a particular class and are inserted into the columns of Table 6 in indented format. With respect to quantity, the main compound classes and content ranges are: parafins (10-22%); isoparafins (20-40%); cycloparafins (3-4%); aromatics (20-40%); and alkenes (5-7%). It was hypothesized that the observed gasoline-heptane difference in pool fire suppression would correlate with the presence of the non-alkane compound groups in gasoline,

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particularly the aromatics. A pool fire suppression experiment was designed where representative compounds from the main classes cited above were selected for 19 cm pool fire extinction evaluation. With the exceptions of *n*-butane and *iso*-pentane the individual compounds in Table 6 were tested as individual fuels and as mixtures ranging from 0 to 40 vol% in heptane for fire suppression using the Siloxane #3 formulation with the 19 cm pool fire apparatus and 1000 ml/min foam flow rate.

Table 6. Compositions of Four Test Fuels based on Chemical Groups

Component Class	Fuel A (%)	Fuel B (%)	Fuel C (%)	Fuel D (%)
Parafins	11.084	14.638	15.568	12.765
n-butane	1.175	1.220	0.887	0.996
n-pentane	0.958	5.173	6.223	6.346
n-hexane	6.557	6.271	6.375	4.646
n-heptane	0.265	0.296	0.220	0.227
n-octane	0.351	0.393	0.249	0.228
n-nonane	0.833	0.668	0.747	0.183
n-decane	0.648	0.319	0.343	0.088
Isoparafins	44.317	28.497	18.535	23.343
i-pentane	5.758	1.892	3.150	2.885
i-octane	13.499	7.108	2.174	9.038
Cycloparafins	4.329	4.527	5.285	3.311
methylcyclopentane	3.226	3.087	3.125	2.291
methylcyclohexane	0.103	0.114	0.085	0.089
Mono-aromatics	18.436	31.428	41.375	41.376
benzene	0.879	0.768	0.804	0.828
toluene	4.362	7.240	10.539	9.366
xylenes	3.762	5.990	7.651	9.516
1,2,4-trimethylbenzene	1.786	4.199	6.355	6.097
Naphthalenes	0.225	0.295	0.225	0.230
Naphthaleon/olefin-benzene	0.319	0.503	0.396	0.402
Indenes	0.538	0.785	0.806	0.697
Mono-naphthalenes	5.231	5.087	5.325	3.310
n-Olefins	6.354	6.214	5.273	6.583
1-hexene	5.548	5.348	4.611	5.930
Isoolefins	0.793	0.761	0.747	0.521
Naphthaleno-olefins	0.099	0.134	0.131	0.089
Oxygenates	11.032	10.504	10.276	10.422

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The fire extinction – fuel composition results are plotted in Figure 11. The results for the aromatic set of compounds (benzene, toluene, xylenes, trimethylbenzene) are remarkable in that 3 of the 4 compounds were not extinguishable as 100% fuels by the Siloxane #3 foam. It had

further been hypothesized that that the vapor pressure of these aromatic compounds would correlate with the time and with foam flow rate needed for extinction (i.e. benzene with its higher vapor pressure would have a larger degrading effect on the foam and a greater permeation through the foam to feed the fire). Just the opposite trend was observed: the difficulty to extinguish is in the order trimethylbenzene > xylenes > toluene > benzene. This unexpected result is further probed by experiments described below. A less pronounced but similarly unexpected trend for difficulty in extinction was observed for the *n*-alkane series: *n*-decane, *n*-nonane > *n*-octane > *n*-heptane > *n*-pentane. It is further noteworthy that within the pair of octanes (*iso*-octane and *n*-octane), *n*-octane was the more difficult fuel fire to extinguish. Finally, the cycloalkanes (methyl cyclopentane and methyl cyclohexane) and alkene (*1*-hexene) pool fires proved to be not significantly more difficult to extinguish than that of heptane. The remarkable features in this series of gasoline-component experiments are the large effects and systematic trend of the aromatic compounds and the effects of *n*-alkane chain length as fuel composition approaches 100%.
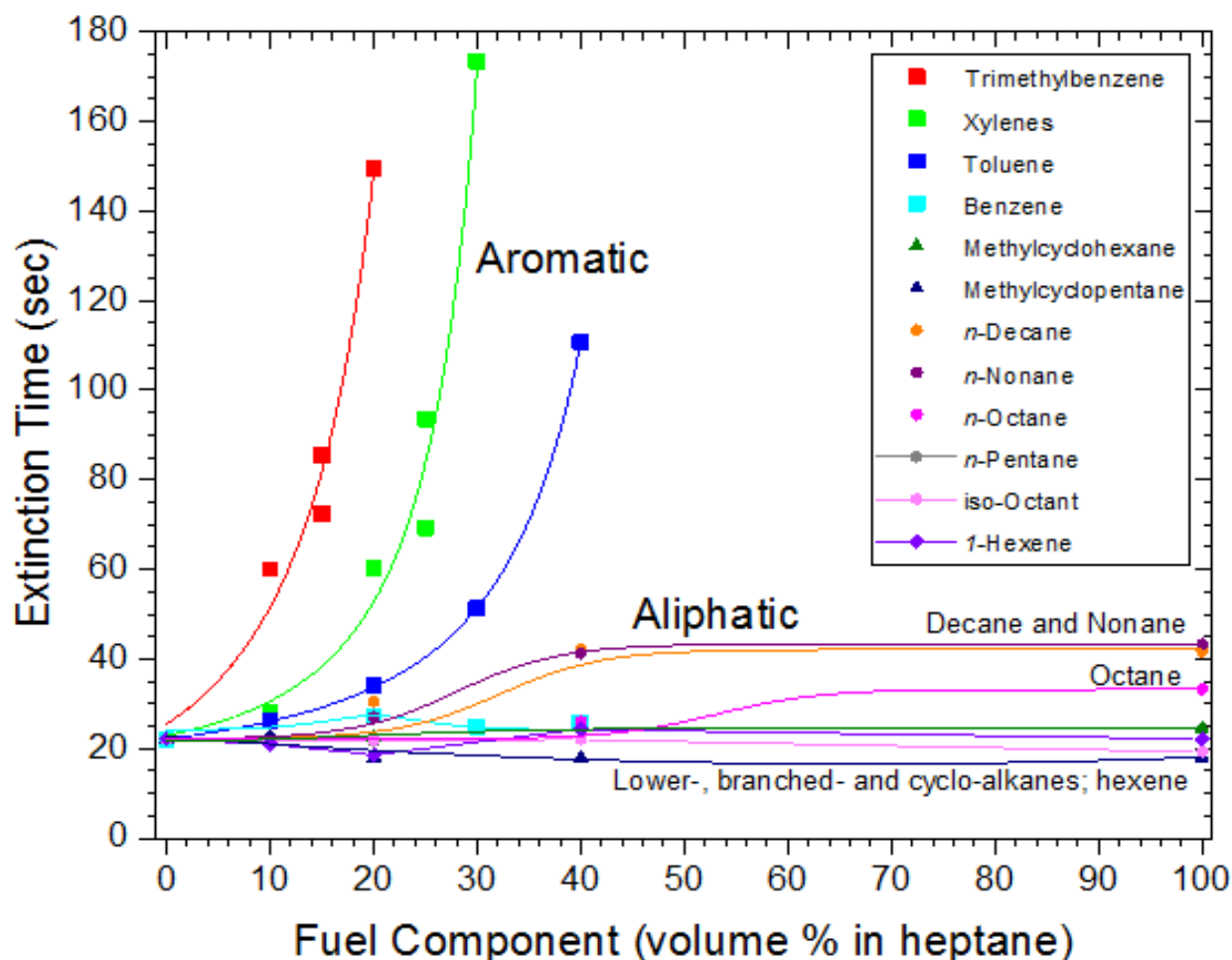

Figure 11. Effect of varying amounts of aromatic and aliphatic gasoline components added to heptane in 19cm pool fire extinction time testing of Siloxane #3 formulation at a constant foam flow rate of 1000 ml/min.

As to the cause of this aromatic component induced behavior and to the order of its effectiveness being opposite to vapor pressure, a hypothesis was directed at the interface between the aqueous surfactant solution and the hydrocarbon fuel with speculation that the fuel component might be crossing the interface to reside in aqueous micelles and thereby reduce the foam stability, or that perhaps one of the surfactants is transporting across the interface to dissolve in the fuel leaving the other surfactant unable to stabilize the foam at this interface. A relatively simple experiment was designed to diagnose such behavior and is illustrated in the Figure 12. It involves ^{1}H NMR spectra to detect transport across the interface between an aqueous solution of the Siloxane #3 surfactants and a hydrocarbon fuel component before and after a short time of contact. A stock solution of 0.5 wt% surfactant(s) in D_2O with a comparable small quantity of dimethyl sulfoxide (DMSO) reference was prepared. A 2.0 ml quantity of the stock solution was placed in the vial; a 670-700 mg sample is withdrawn for a control spectrum; a gasoline component is gently added for a 1-2 mm upper phase thickness with minimum perturbation of the interface; the aqueous phase is slowly stirred (no vortex formation) for 5.0 min; and a second 670-700 mg sample of the aqueous phase is collected via syringe from the bottom of the vial for NMR analysis. The experiments include stock solutions of 502W, Glucopon 225DK and a 1:1 502W:Glucopon 225DK surfactant mixture and gasoline components of 1,2,4-trimethylbenzene (TMB), xylenes (Xyls), toluene (Tol), benzene (Bz), n-decane ($C_{10}H_{22}$), n-heptane (C_7H_{16}) and n-pentane (C_5H_{12}). Some spectral features are unique to a surfactant (e.g. Si-CH$_3$) or to a gasoline component (e.g. Ar-H) and other features have two or more contributors (e.g. –O-CH$_2$- from both surfactants). In the spectrum these features or resonances are integrated and normalized to the DMSO resonance. In Table 7 is a correlation of spectral features with the chemical shift range, structural assignment and the corresponding components. Spectra of individual surfactants and gasoline components with resonance assignments are presented in Appendix C with a table of integrated values.
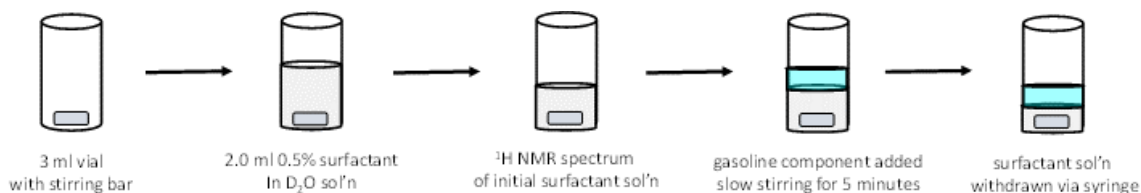

Figure 12. Depiction of simple NMR experiment to probe transport across the aqueous surfactant solution – hydrocarbon interface.

Table 7. 1H NMR Resonance Chemical Shift – Structure Correlation

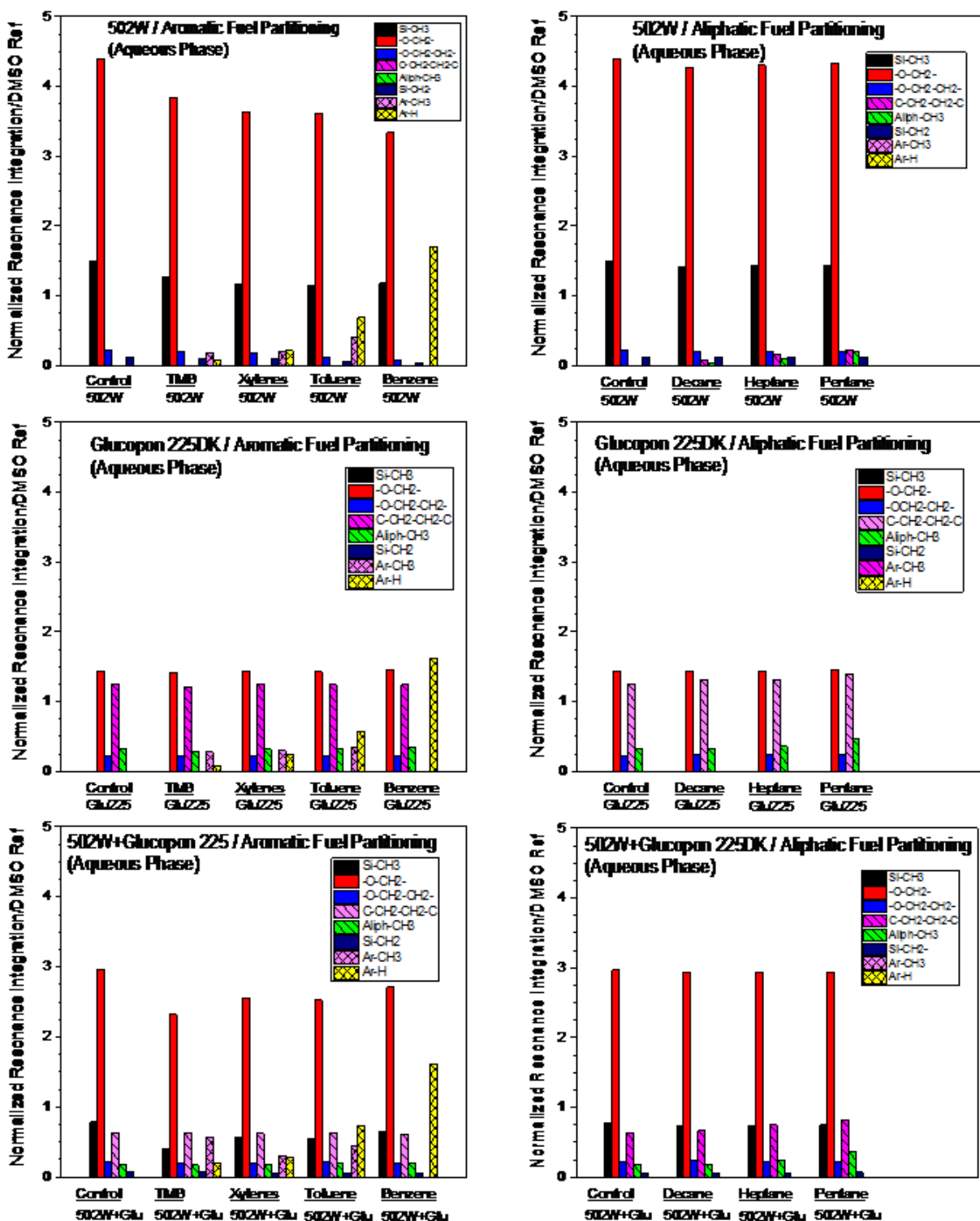| Chem Shift	Assisgnment	Corresponding Component
0.0 – 0.2 ppm	Si-CH3	502W
3.2 – 4.0 ppm	-O-CH2-	502W, Glucopon
1.5 – 1.7 ppm	-O-CH2-CH2-	502W, Glucopon
1.2 – 1.4 ppm	C-CH2-CH2-C	Glucopon, Aliphatic Gas Component
0.8 – 1.0 ppm	Aliph-CH3	Glucopon, Aliphatic Gas Component
0.4 – 0.5 ppm	Si-CH2-	502W
1.8 – 2.1 ppm	Ar-CH3	Aromatic Gas Component
6.5 – 6..8 ppm	Ar-H	Aromatic Gas Component

Figure 13. Synopsis of ^{1}H NMR results of surfactant and gasoline component diffusion across the aqueous-organic interface.

In this table there is a color and pattern code which is used in a bar graph depiction (Figure 13) of surfactants and gasoline components transporting across the aqueous-organic interface. The solid colors without pattern denote surfactant only resonances; the parallel line pattern denotes overlapping resonances from a surfactant and a gasoline component; and the cross-hatched pattern denotes gasoline component resonances only. All of the transport experiments are summarized in the form of bar graphs in Figure 13. There are six bar graphs arranged in two columns and three rows. For comparative purposes the column on the left represents the aromatic gasoline component experiments, and that on the right represents the aliphatic gasoline component experiments. The three rows correspond to different surfactant solutions; the top row is 502W only, the middle row is Glucopon 225DK only and the bottom row is the 1:1 502W:Glucopon 225DK surfactant combination. Within an individual series of bar graphs, the control experiment is on the left representing the surfactant solution prior to interface contact with the gasoline component, and the subsequent groupings to the right progress from least volatile to most volatile gasoline component. The intent in this design is to identify systematic trends for surfactant and gasoline component interface crossing.

One way to interpret the data in Figure 13 is to start with the relatively simple aromatic and aliphatic gasoline components. In the left column of bar graphs there is a progression of yellow (Ar-H) and pink (Ar-CH3) that increase in height as one proceeds from TMB to Bz indicating an increasing quantity of aromatic component crossing the interface into the aqueous phase. There is a parallel with these components' solubility in water: Bz (0.178%) > Tol (0.0515%) > Xyls (0.0187%) > TMB (0.0057%). By comparison in the right column of bar graphs, the aliphatic components (purple parallel line pattern (C-CH2CH2-C) and green parallel line pattern (Aliph-CH3)) display a low transport into the aqueous phase. This is particularly visible in the top right bar graph where there is no Glucopon to contribute to these aliphatic component column heights. The relative amounts of aliphatic component in the aqueous phase also parallels these components' solubility in water: C5H12 (0.0038%) > C7H16 (0.00029%) > C10H22 (0.0000052%). While the amount of aromatic components transferring to the aqueous phase is substantially greater than that for the aliphatic components and the aromatic component also has a pronounced increasing effect on extinction time compared to the aliphatic component, the order of this increased extinction time (TMB > Xyls > Tol > Bz) is opposite to that for aqueous transfer (Bz > Tol > Xyls > TMB). This appears to indicate that diffusion of aromatic components into the aqueous phase <u>does not</u> have a retarding effect on the 502W-Glucopon 225DK formulation's pool fire extinguishing activity.

The data in Figure 13 provide an interesting insight into diffusion of the surfactant from the aqueous into the organic phase. Comparing the 502W data (particularly black and red bars relative to the controls) in the first row, the amount of diffusion into an aromatic phase is much higher than into an aliphatic phase. Within the aromatic components, 502W displays more interface diffusion for Bz than for TMB. In the second row the interface diffusion behavior for Glucopon 225DK is noteworthy for its lack of diffusion as indicated by the constant height of its red bar. However for the 1:1 502W:Glucopon 225DK in the third row, the aromatic phase diffusion activity of the 502 surfactant is altered with the amount now for TMB greater than that

for Bz as is evident from comparison of the 502W exclusive black bar data. Surfactant diffusion toward the aliphatic phase is nominal as is the case for the individual surfactants in the upper rows.

The result of significance from these interface transfer experiments is that diffusion of the 502W surfactant from the aqueous to the aromatic organic phase is substantial. When 502W is combined with Glucopon 225DK in a 1:1 formulation, its diffusion out of the aqueous phase is the greatest for TMB in the aromatic component series. This result correlates with the pool fire extinction results in Figure 11. A speculated scenario is that 502W when combined with Glucopon 225DK at the aqueous-organic interface is more prone to cross this interface into the receptive aromatic environment. Its departure from the 502W-Glucopon aqueous foam structure at the foam-fuel interface destabilizes the foam and thus diminishes the ability of this formulation to extinguish pool fires. This speculation can lead to hypothesizing about doing something to 502W that would make it less prone to cross an aqueous interface into an aromatic-hydrocarbon medium. This speculation may also be applied to the hydrocarbon surfactants in the other F3 formulations although their proprietary identities impede experimental verifications.

Two-Component Simulant for Gasoline

From the foregoing results, it is clear that the aromatic components in gasoline are responsible for a pool fire suppression behavior that diverges from that of heptane when foams generated from F3 formulations are used. Of the aromatic components investigated, 1,2,4-trimethyl-benzene is the most effective. In this section data are presented to support the possibility of designating a two-component simulant for commercial alcohol-free unleaded gasoline. As indicated in the previous section, gasoline is a very complex mixture of over 100 hydrocarbon components with seasonal and source variations. If it is possible to formulate a two component mixture from heptane and an aromatic counterpart that will effectively simulate a general F3 formulation's extinction performance with the gasoline pool fire, it could be a very useful and simple reference fuel for a testing protocol. A substantial body of data is needed to validate the concept of a gasoline simulate. Presented below are foam degradation and extinction data for the fluorine-free Siloxane #3 formulation and for the RefAFFF formulation to represent this concept's initial viability. Operational viability would, of course, require a much broader base of data and large scale field testing.

Foam degradation data were obtained by monitoring the time-dependent reduction of a 4 cm layer of foam deposited onto a 60 mL volume of 60°C preheated fuel in a 150 mL beaker. For the Siloxane #3 foam, its degradation over heptane, gasoline and the comparative effects of adding 15 and 25% TMB to heptane are depicted in Figure 14. The 15% TMB data represent intermediate behavior in the foam height vs time plot for the 4 cm layer of foam to disappear. Increasing the TMB content to 25% results in a foam degradation time coincident with that for gasoline. The degradation effect of this 25% TMB/heptane fuel on RefAFFF foam is presented in Figure 15. The rapid decrease in foam height occurs at an intermediate time (130-140 sec) compared with that for the heptane (160-180 sec) and the gasoline (100-120 sec). In this case the foam degradation is accelerated by the 25% TMB but does not match that produced by the gasoline.
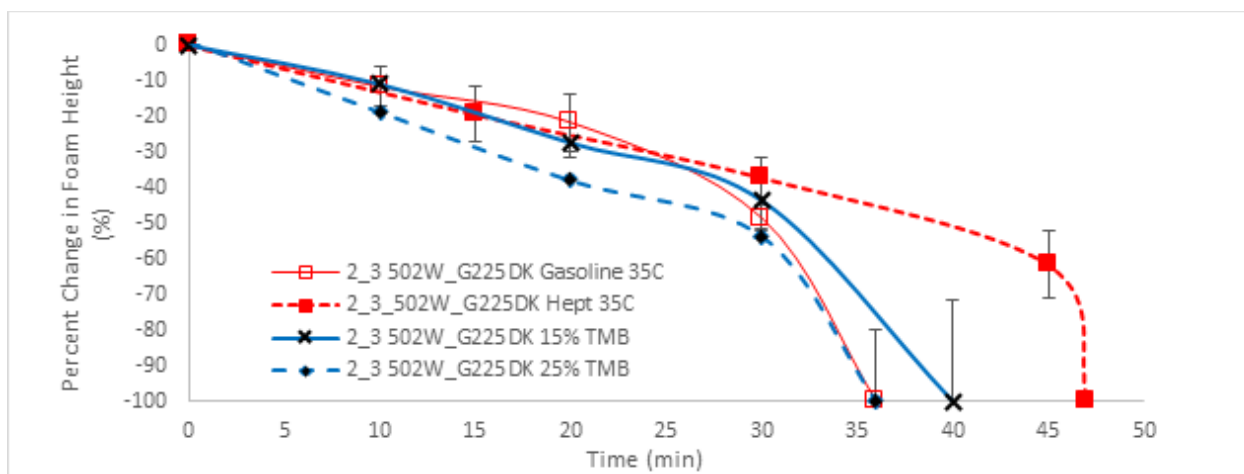
Figure 14. Degradation of a 4 cm Siloxane #3 foam layer over gasoline, heptane and combinations of 15 and 25% TMB/heptane at 35°C.
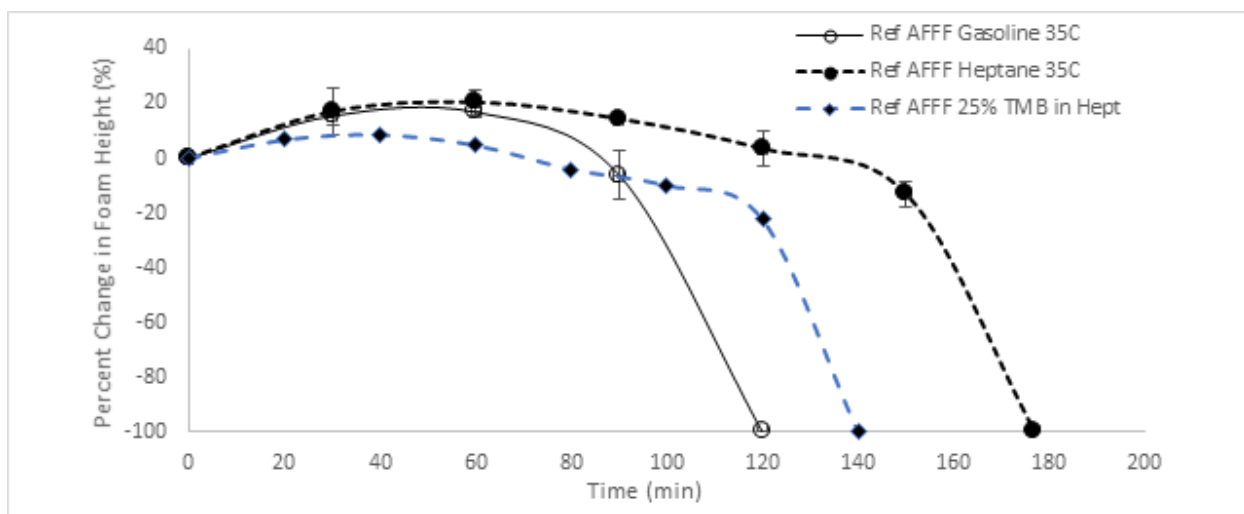

Figure 15. Degradation of a 4 cm RefAFFF foam layer over gasoline, heptane and a 25% TMB/heptane fuels at 35°C.

The 25% TMB/heptane fuel composition's effect on the Siloxane #3 formulation's pool fire extinction time compared with the gasoline and heptane fuels is presented in Figure 16. As previously indicated (Figure 5), this F3 silicone formulation's ability to extinguish gasoline fires is much diminished compared with heptane fires, and the data presented in Figure 16 were obtained at a foam flow rate where extinction was accomplished on both fuels. The 25% TMB/ heptane fuel fire extinction by the Siloxane #3 formulation is in reasonably close proximity (about 90 sec) to that for gasoline (average 110 sec) and significantly removed from that for heptane (17 sec). As a two-component simulant for gasoline, these data indicate the 25% TMB/ heptane is a good candidate for further benchtop and large scale testing.
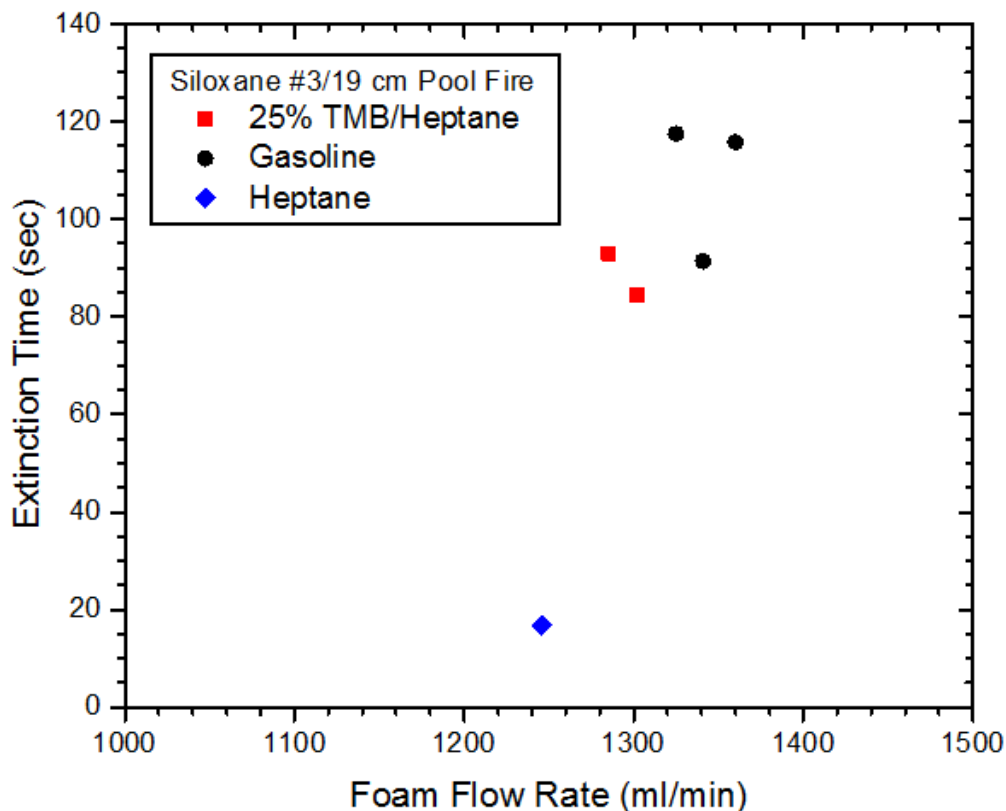
Figure 16. Comparison of extinction times for 25% trimethylbenzene/heptane fuel vs gasoline and heptane fuels using the Siloxane #3 formulation and the benchtop 19 cm pool.

DISCUSSION

In this report the objective is to disclose an unexpected finding where the difference in suppression of gasoline and heptane pool fires was very large for an experimental silicone surfactant based F3 formulation. Testing of commercial F3 formulations also displayed a less but similar difference in capability to extinguish gasoline vs heptane fires while AFFF formulations were relatively insensitive to the fuel identity. An anticipated revision of MIL-F-24385F with a pool fire fuel change from gasoline to heptane is the impetus for composing this report. In this section some thoughts are offered with regard to its cause and to current and future implications of this unexpected finding.

Gasoline vs heptane fire suppression should be further investigated with a broader collection of F3 formulations and at both the benchtop and MilSpec scale to better define a metric of difference for gasoline and heptane fire extinctions. Gasoline's complex and variable composition makes it a difficult standard to rely upon. We think continued use of gasoline as a standard will become more problematic with increasing testing of F3 formulations. However, a switch to heptane as the reference may result is some F3 formulations being qualified and then later lacking anticipated performance when being used by firefighters on gasoline fires. If a diagnostic qualification test could be performed with a compositionally defined simulant for gasoline for F3 formulations, it might serve as a qualifying metric for gasoline fires. Our finding

that the aromatic components in gasoline, particularly trimethylbenzene, are a cause for less effective fire suppression by F3 formulations, may offer the possibility of developing a simple two component (trimethylbenzene + heptane) simulant for gasoline. Along with additional fire suppression testing, it could also be further investigated with analyses of surfactant and fuel components crossing the aqueous surfactant solution – fuel interface as described above and in Figures 12 and 13. Also, the possibility of separate MilSpec standards for AFFF and F3 formulations has been heard to be a possible consideration.

Looking toward the future, two important premises in trying to develop new F3 formulations to replace AFFF formulations are: (1) Mechanisms of foam activity for pool fire suppression are fundamentally different for AFFF and F3 based foam formulations; and (2) Effectiveness of fuel fire suppression by F3 formulations is dependent on the identity of the fuel, with the gasoline fire being the more difficult to extinguish while fuel fire suppression by AFFF formulations is relatively insensitive to the identity of the fuel. These two premises are derived from the unique properties that the incorporation of a sufficient quantity of fluorine into a surfactant tail structure provides to an aqueous foam. These properties include: a low polarizability which translates into an exceptionally low surface tension; an oleophobicity that repels hydrocarbons; and an exceptionally high thermal and chemical stability conferred to the fluorine-carbon bond that resists degradation in a burning salt water environment. Finding/designing a fluorine-free surfactant that can deliver comparable properties to an F3 formulation is a monumental challenge. However, mimicking the fluorocarbon surfactant is not the only route to an effective fire suppressing foam formulation. If effective fire suppression is obtained from a foam based on non-fluorocarbon components, the properties of such a foam and its concentrate will be substantially different from those of AFFF formulations. Further, if a different chemistry is successful, the specifications for its effectiveness should be tailored to those F3 capabilities and composition and not to the AFFF MilSpec which was written to fit fluorocarbon surfactant based formulations. New approaches to and limitations of F3 formulations along with suggestions for future development are described in the balance of this discussion section.

New approaches to F3 formulations should be tempered with the lesson from fluorocarbon surfactant history summarized in the introduction. It involved very difficult chemistry of an unutilized element, acceleration to a technology as a critical component of the Manhattan Project and development of a business driven array of new products. Three general approaches are described below: new classes of surfactants; surfactant synergisms; environmentally acceptable fluorosurfactants.

Today, discovering new classes of surfactants beyond the hydrocarbon, silicone and fluorocarbon categories will involve significant out-of-the-box thinking and chemistry, particularly if one tries imitate some of the fluorocarbon surfactant's more important properties. Combined oleophobicity/hydrophobicity and low surface tension are key properties. Pursuing such properties via an inorganic and nanoparticulate surfactant route could prove interesting [48].

Synergisms between interacting surfactants can produce properties beyond the range of those possessed by the individual surfactants. The 1993 patent by Norman and Regina that combined

an alkyl polyglycoside surfactant with a fluorocarbon surfactant resulted in very large fire suppression enhancements enabling a significant reduction in quantity of fluorocarbon used along with a significant cost reduction for the formulation [40]. Since then, alkyl polyglycosides have been reported to have synergisms with other surfactants [49] but the mechanism for such effects remains unknown. As a tool for further advancement in fire suppression performance of fluorine-free foam formulations, an understanding of the surfactant molecular interactions that promote useful increases in desired properties would be very beneficial.

Environmentally acceptable fluorosurfactants are those which are susceptible to biodegradation without being toxic themselves or in their biodegradation products. If sufficient fluorosurfactant properties important for fire suppression can be maintained while incorporating a sufficient susceptibility to biodegradation and a non-toxicity, this approach of retaining some fluorine in the surfactant structure may have significant merit. This involves the preparation of surfactant tail structures where the fluorocarbon -CF_2- chain is interrupted with -CFH- and -CH_2- moieties [50, 51]. Rigorous biodegradation and toxicity testing would be needed in addition to creative and challenging chemistry.

SUMMARY

Gasoline and heptane, as fuels for evaluation of firefighting foam capability, have been comparatively tested with three AFFF formulations (one experimental and two commercial) and five fluorine-free formulations (one experimental and four commercial) at benchtop scale. The AFFF formulations are relatively insensitive to the identity of the fuel, but the F3 formulations display a significant divergence in extinction capability between these two fuels with the gasoline fire being the more difficult to extinguish. Using the most sensitive F3 formulation (Siloxane #3), twelve major components of gasoline from the *n*-alkane, *iso*-alkane, *cyclo*-alkane, aromatic and olefin categories were examined to determine a source for this difference in extinction capability by the fluorine-free formulations with the finding that it is the aromatic components category. Within the aromatic components this effect substantially increased with the number of methyl substituents (trimethylbenzene > xylenes > toluene > benzene). The mechanism involved was investigated by an experiment monitoring the aqueous surfactant solution – fuel interface for the crossing of surfactants into the fuel phase and fuel components into the aqueous phase with the finding that the degree of extraction of surfactant into the fuel correlated with the effect of the fuel component on extinction, particularly within the aromatic components (trimethylbenzene > xylenes > toluene > benzene). As a simple two-component simulant for gasoline, a trimethylbenzene/heptane mixture is proposed and supported by foam degradation and fuel vapor transport through the foam characterization. From these results, it is proposed that further work be conducted on the gasoline vs heptane pool fire extinction evaluation of fluorine-free foam formulations and that testing with a well-defined gasoline simulant be considered to complement heptane pool fire suppression evaluation.

ACKNOWLEDGEMENT

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APPENDIX A

Non-volatiles profiles were determined for the AFFF and F3 concentrates by subjecting an initial 600mg quantity of concentrate to 12 hr periods of reduced pressure treatments with successive recording of residual mass and increments in vacuum.
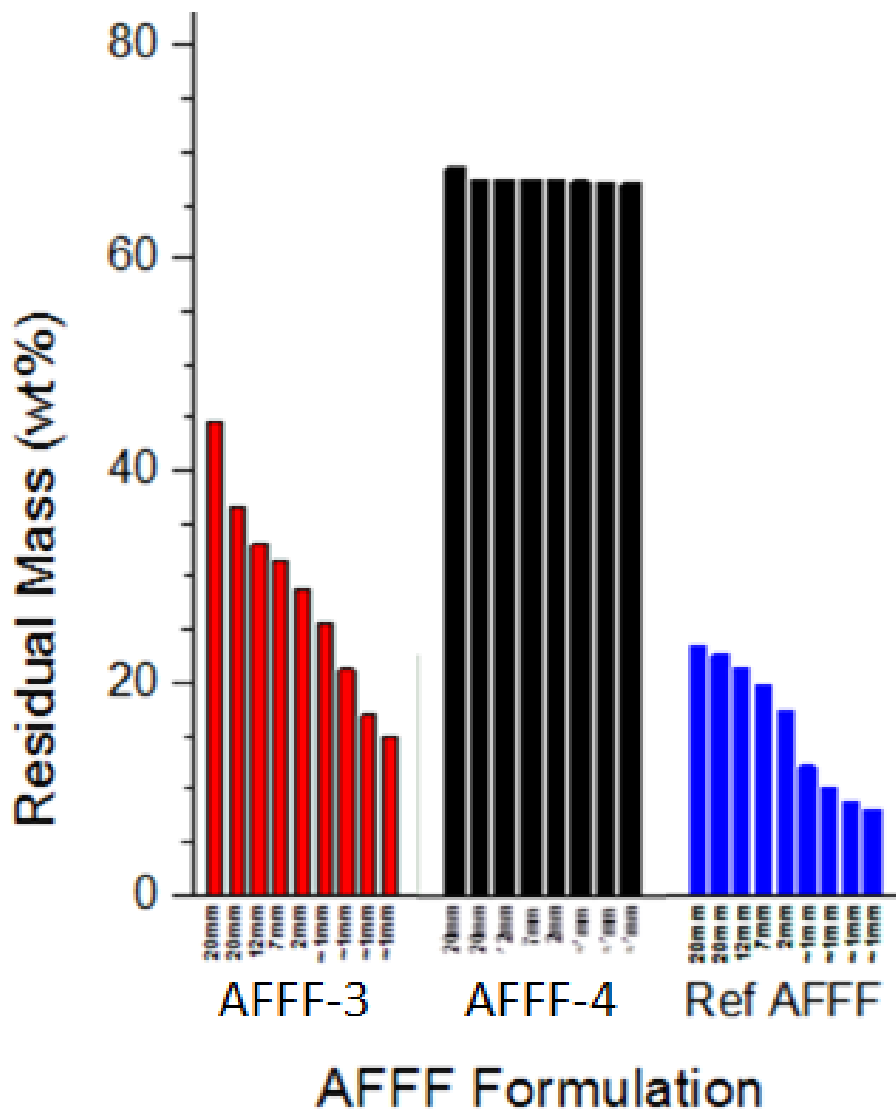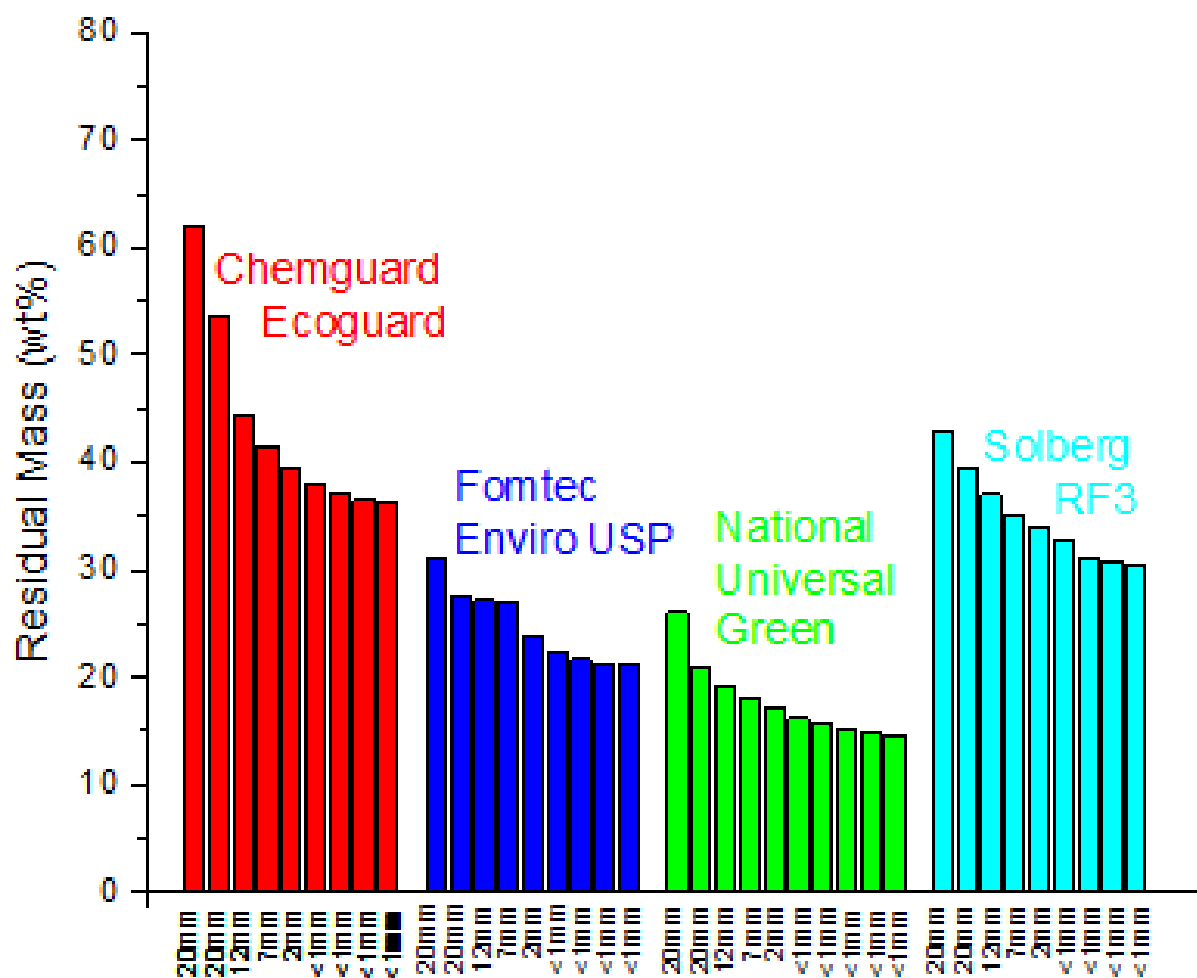

Figure A1. Non-volatiles profile of RefAFFF concentrate [38] and AFFF commercial concentrates AFFF-3 and AFFF-4.

Figure A2. Non-volatiles profile of F3 commercial concentrates: Chemguard Ecoguard 3% F3 (Chemguard, Ltd.); Fomtec Enviro ARC 3x6 (Dafo Fomtec AB) (Fomtec); National Foam Universal Green 3-3% Alcohol Resistant Synthetic Foam Concentrate (National Foam); Solberg Re-Healing Foam RF3% (Solberg Scandinavian AS).

APPENDIX B

^{1}H NMR Spectra of F3 Commercial Concentrates.

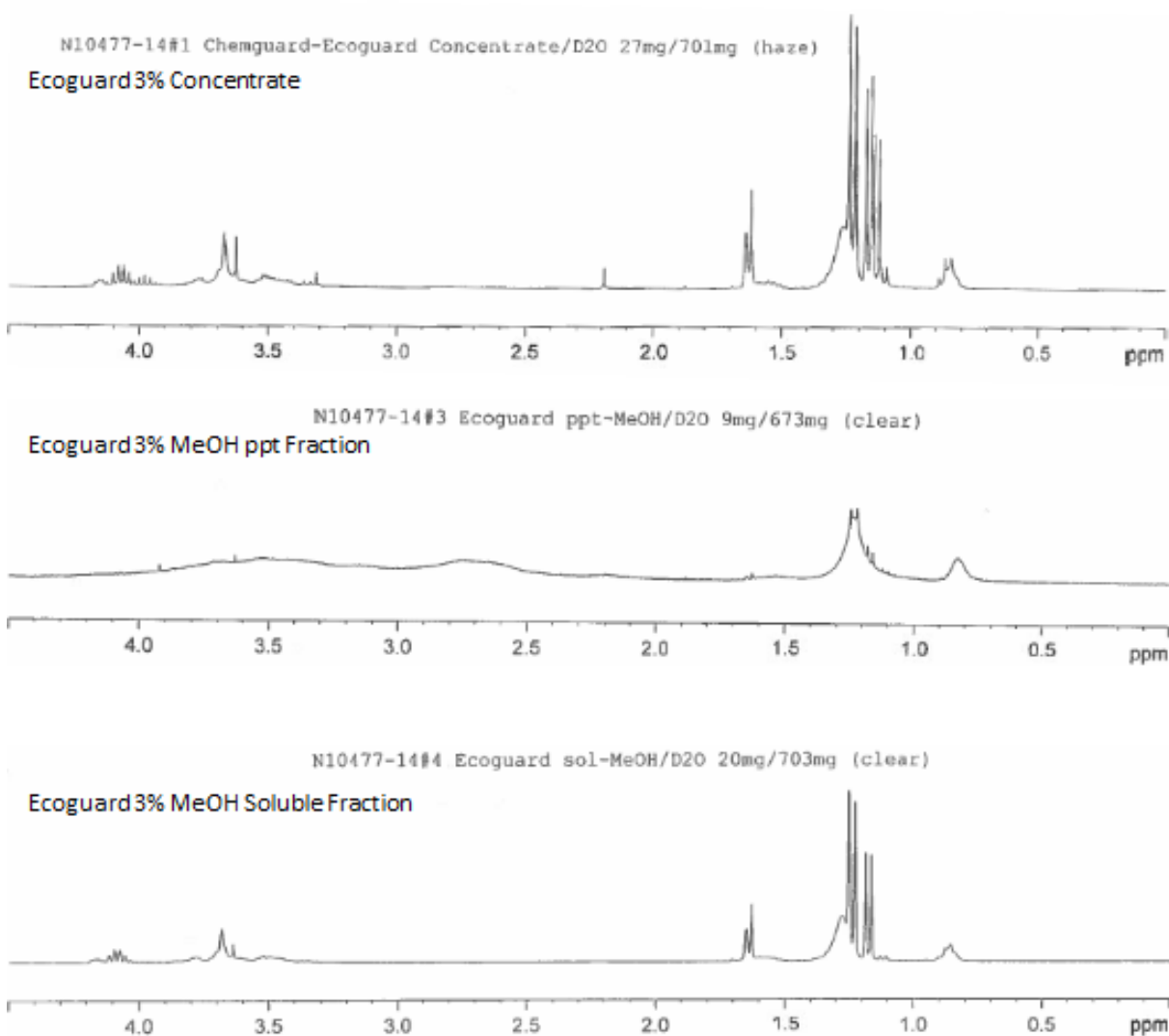N10477-14#1 Chemguard-Ecoguard Concentrate/D2O 27mg/701mg (haze)
Ecoguard 3% Concentrate

N10477-14#3 Ecoguard ppt-MeOH/D2O 9mg/673mg (clear)
Ecoguard 3% MeOH ppt Fraction

N10477-14#4 Ecoguard sol-MeOH/D2O 20mg/703mg (clear)
Ecoguard 3% MeOH Soluble Fraction

Figure B1. ^{1}H NMR spectra of Chemguard Ecoguard 3% F3: top spectrum - 3% concentrate in D_2O; middle spectrum - CH_3OH insoluble fraction in D_2O; bottom spectrum - CH_3OH soluble fraction in D_2O.
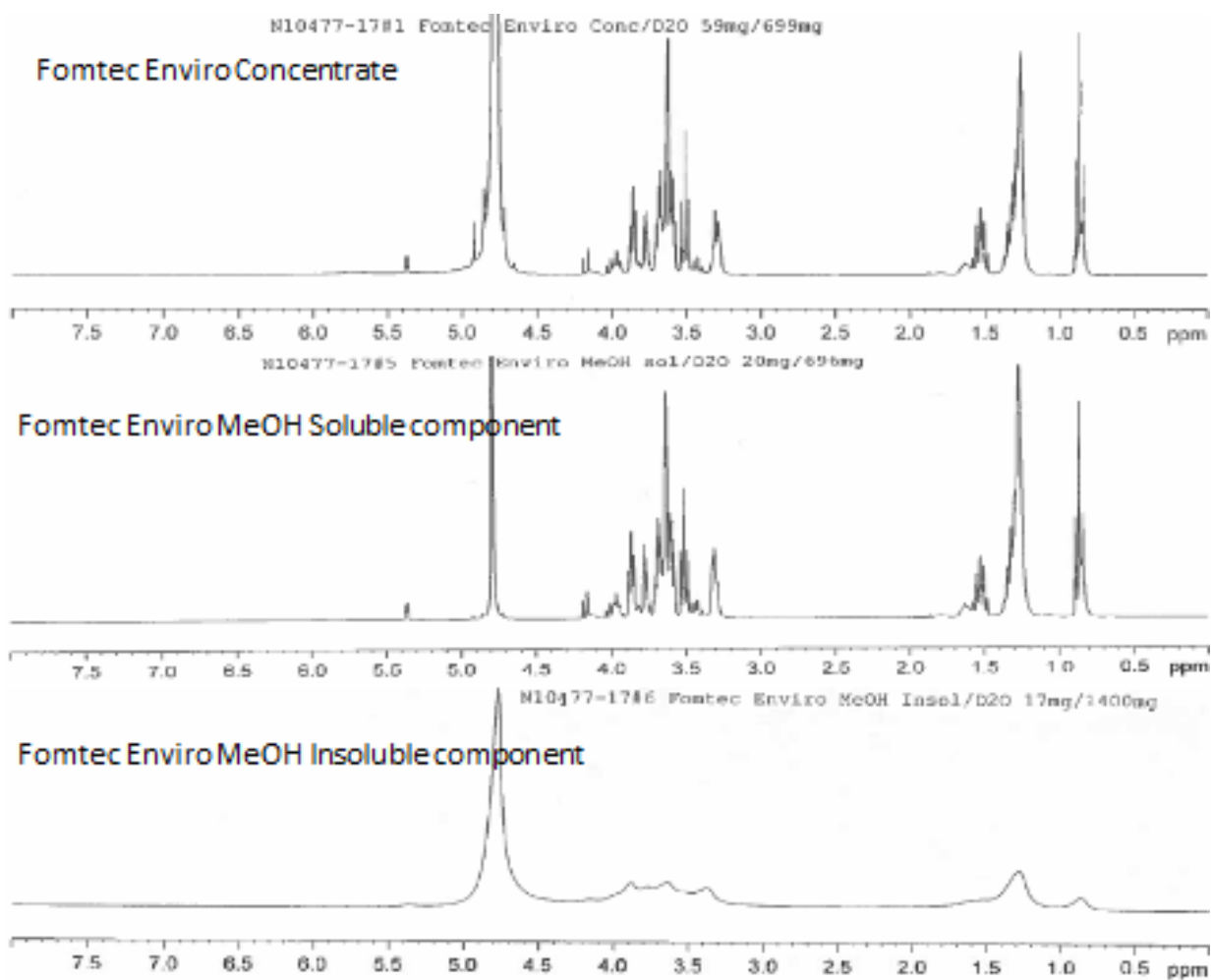
Figure B2. ^{1}H NMR spectra of Fomtec Enviro ARC 3x6: top spectrum - 3% concentrate in D_2O; middle spectrum - CH_3OH soluble fraction in D_2O; bottom spectrum - CH_3OH insoluble fraction in D_2O.

National Universal Green Concentrate

National Universal Green MeOH soluble

National Universal Green MeOH insoluble 3mg/759mg
Very viscous, near clear

National Universal Green MeOH insoluble diluted to 3mg/1450mg
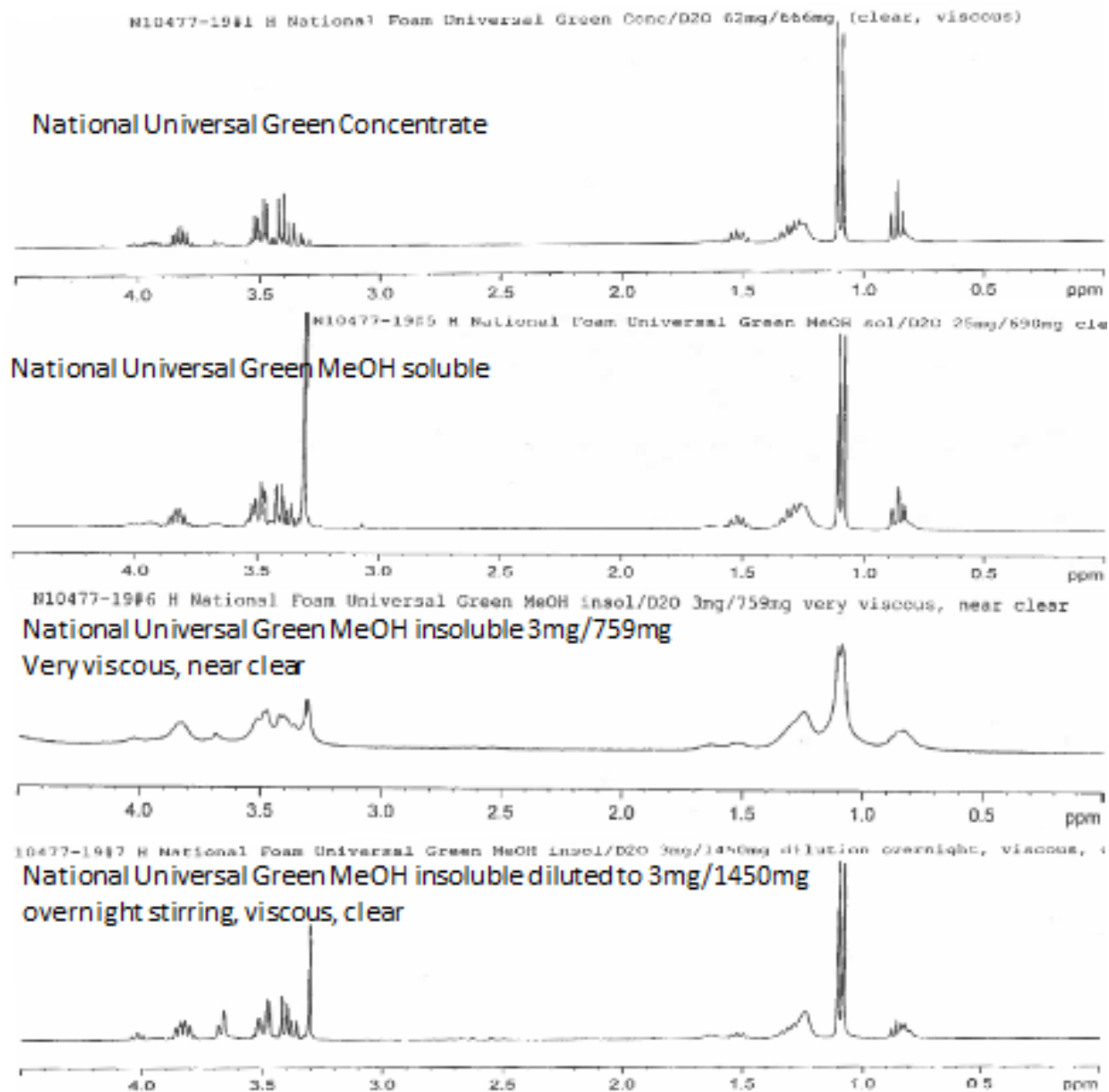overnight stirring, viscous, clear

Figure B3. ^{1}H NMR spectra of National Foam Universal Green 3-3% Alcohol Resistant Synthetic Foam Concentrate: top spectrum - concentrate in D_2O; second spectrum - CH_3OH insoluble fraction in D_2O; third spectrum - CH_3OH insoluble fraction in D_2O; fourth spectrum – insoluble fraction in D_2O diluted.

APPENDIX C

This appendix contains experimental ^{1}H NMR spectra of the siloxane #3 surfactants and the gasoline component additives (Bz, Tol, Xyls, TMB, pentane, heptane and decane) used in the aqueous surfactant – fuel component interface transport experiment connected with Figure 13.
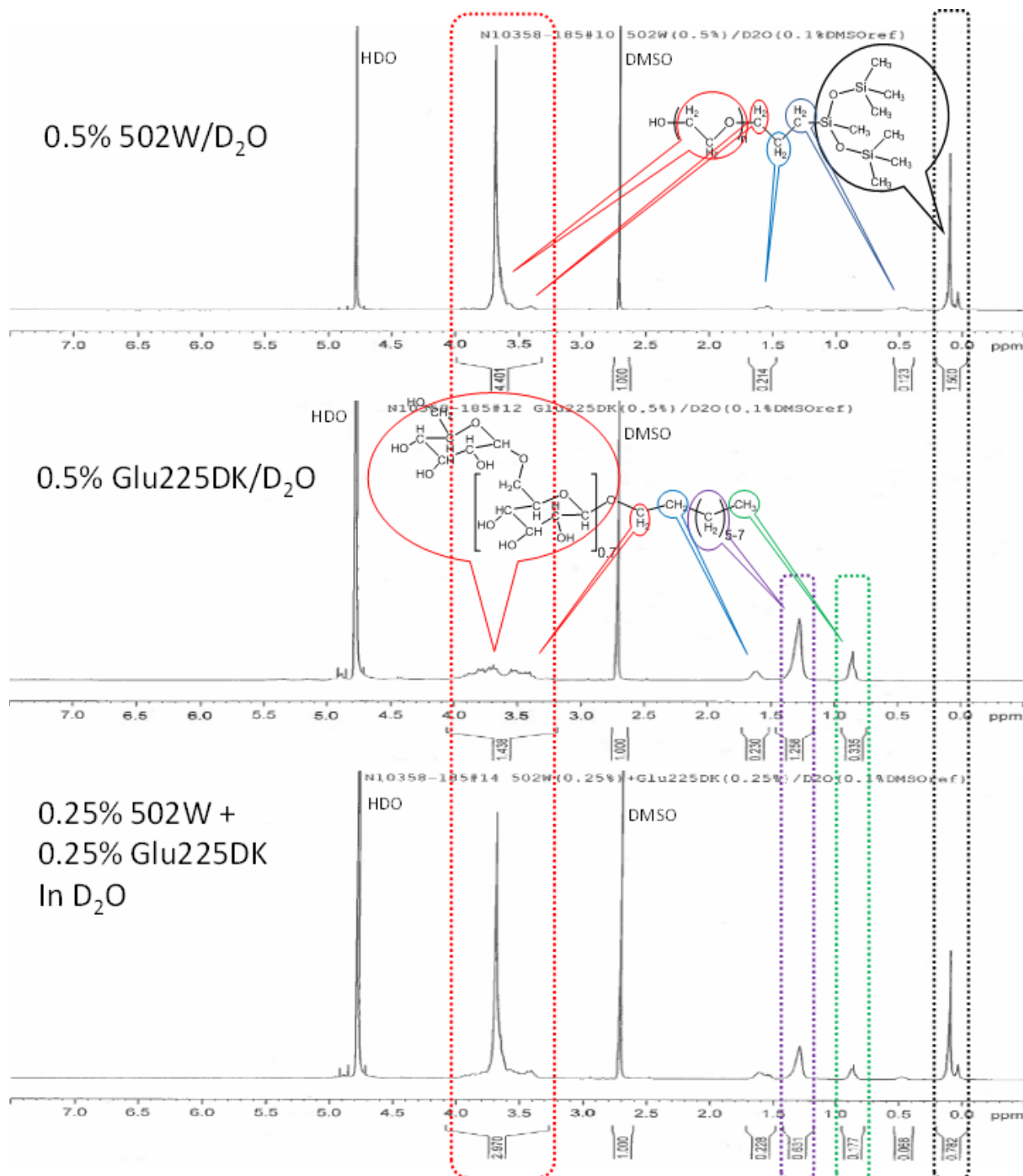

Figure C1. Integrated ^{1}H NMR spectra of the 502W, Glucopon 225DK and the 1:1 combination of these surfactants with assignments indicated.
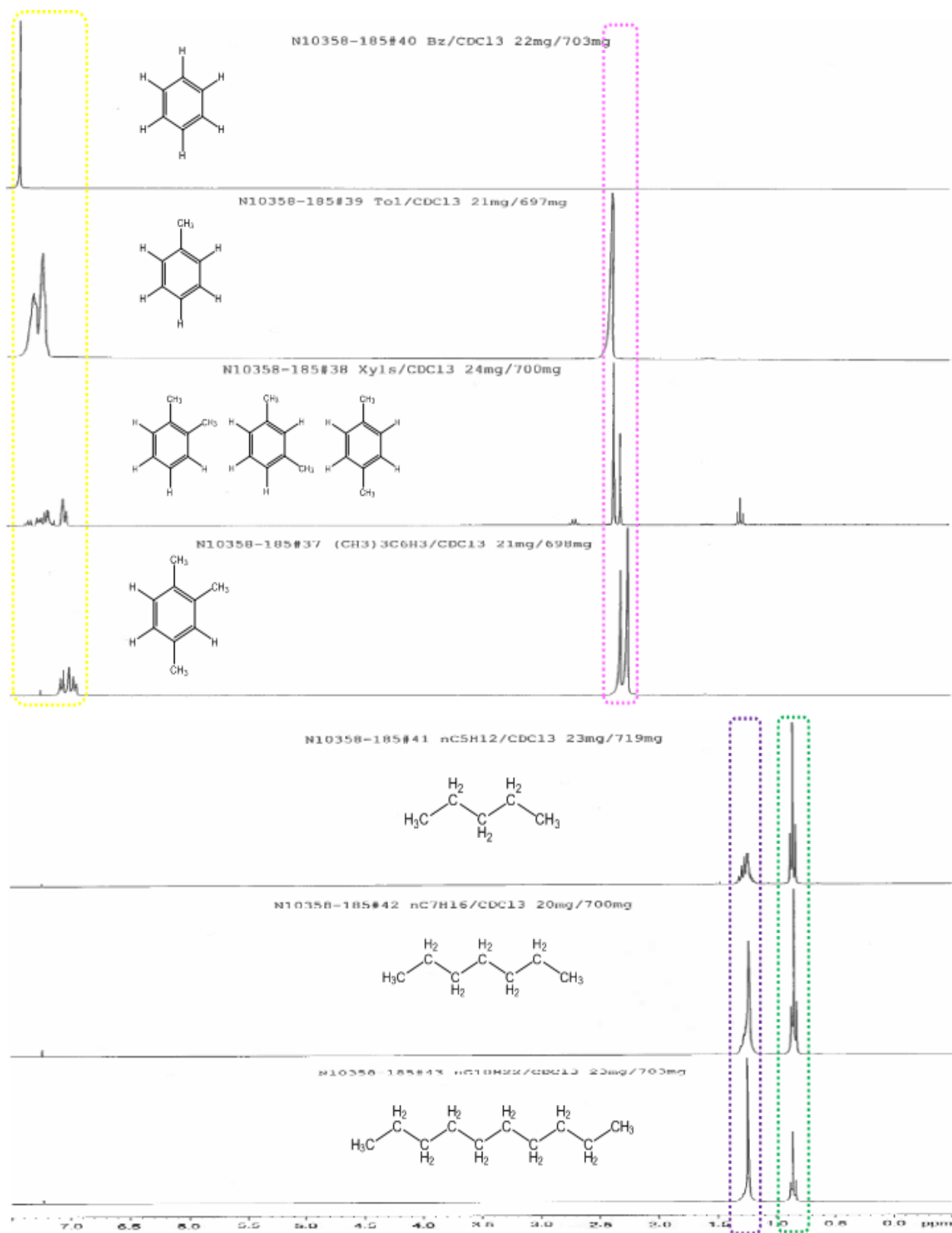
Figure C2. ^{1}H NMR spectra of the aromatic (benzene, toluene, xylenes and 1,2,4-trimethyl-benzene) and aliphatic (pentane, heptane and decane) gasoline components in CDCl$_3$ solution.

Figure C3. Integrated ^{1}H NMR spectra of the D$_2$O phase of 502W, Glucopon 225DK and the 1:1 combination solutions after 5.0 minutes contact with TMB and low speed stirring.
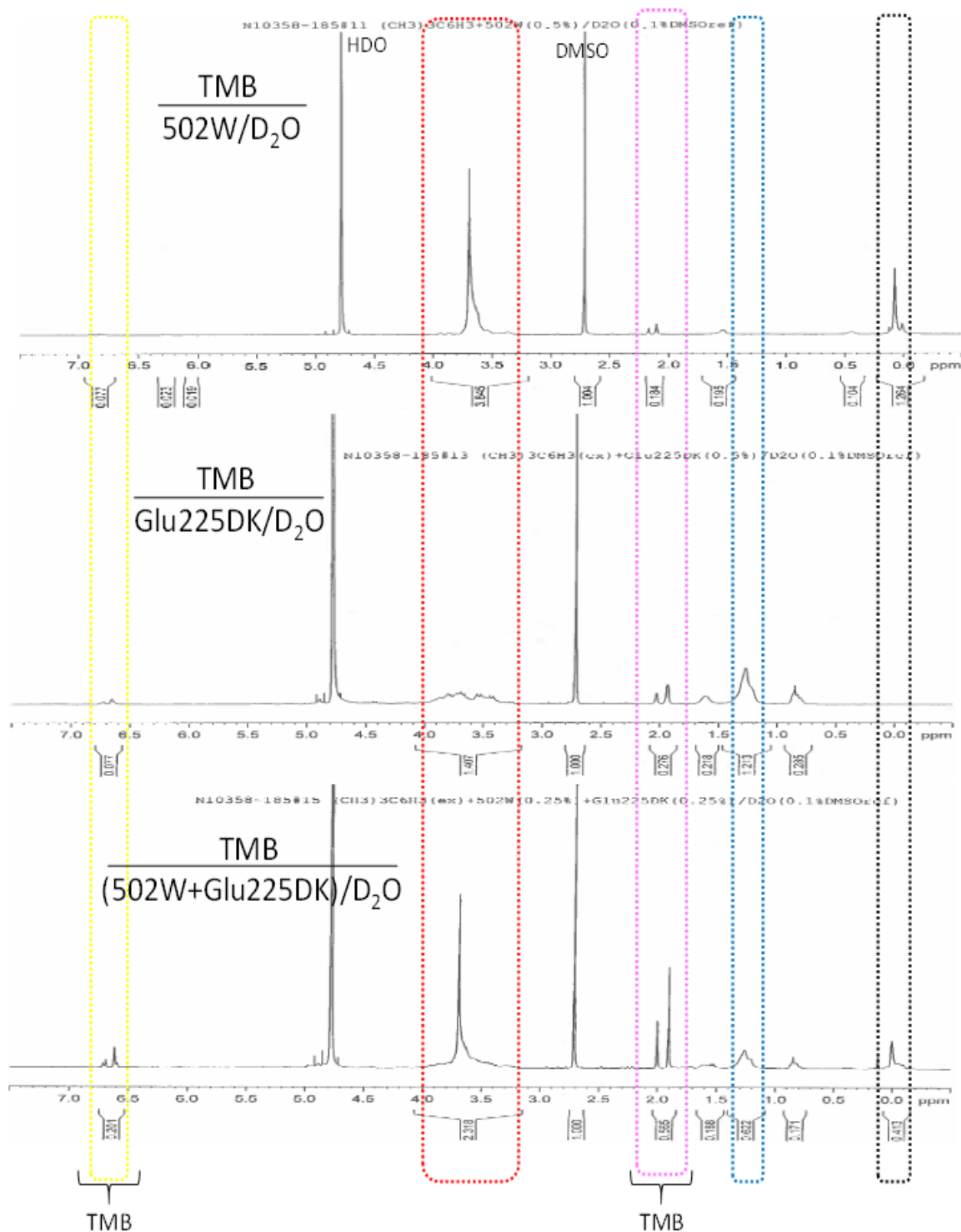
Figure C4. Integrated ^{1}H NMR spectra of the D$_2$O phase of 502W, Glucopon 225DK and the 1:1 combination solutions after 5.0 minutes contact with pentane and low speed stirring.
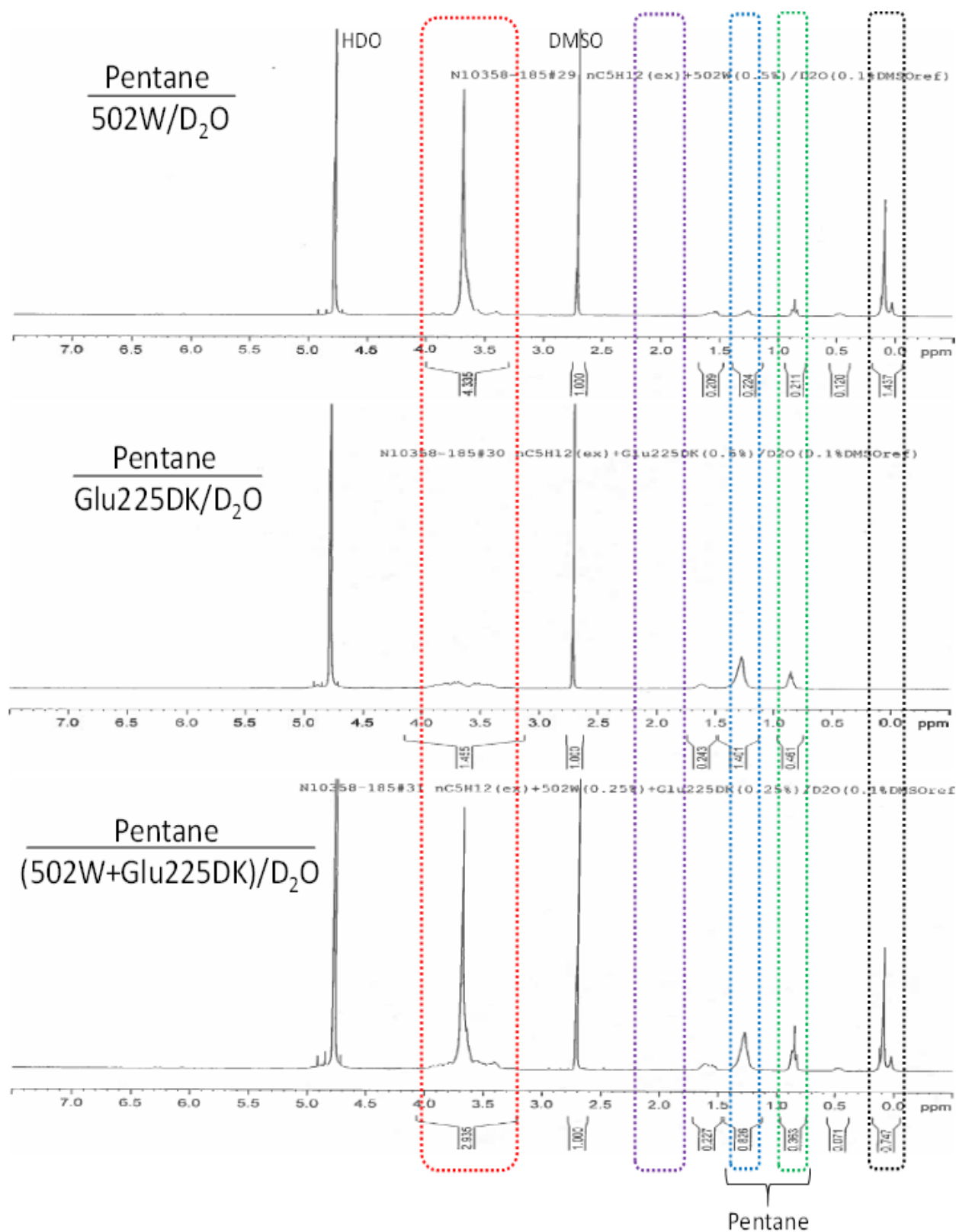
Table C1. Integrated Spectral Data Relative to DMSO Reference for Experimental Measurement of Surfactant and Gasoline Component Transport across the Aqueous-Organic Interface (Spectrum #'s have NRL Laboratory Notebook citation N-10358 pp 185-195, and numerical data under assigned structures represent corresponding resonance peak area integrations within ppm range specified and normalized to DMSO resonance.)

Spectrum #		$Si-CH_3$ $0.2 \rightarrow 0.0$	$-O-CH_2-$ $4.1 \rightarrow 3.3$	$-O-CH_2-\underline{CH_2}-$ $1.75 \rightarrow 1.55$	$C-CH_2-CH_2-C$ $1.4 \rightarrow 1.2$	$Aliph-CH_3$ $1.0 \rightarrow 0.8$	$Si-CH_2-$ $0.5 \rightarrow 0.4$	$Ar-CH_3$ $2.1 \rightarrow 1.8$	$Ar-H$ $6.8 \rightarrow 6.5$
502W	#10	1.500	4.401	0.214			0.123		
502W+TMP	#11	1.264	3.845	0.195			0.104	0.184	0.077
502W+Xyls	#16	1.173	3.629	0.182			0.090	0.204	0.213
502W+Tol	#19	1.155	3.615	0.125			0.066	0.413	0.689
502W+Bz	#22	1.185	3.334	0.080			0.048		2.442
502W+C10	#32	1.404	4.263	0.209	0.076	0.038	0.117		
502W+C7	#26	1.436	4.302	0.211	0.161	0.097	0.119		
502W+C5	#29	1.437	4.335	0.209	0.224	0.211	0.120		
Glu225	#12		1.438	0.230	1.258	0.335			
Glu225+TMP	#13		1.407	0.218	1.213	0.285		0.276	0.077
Glu225+Xyls	#17		1.436	0.224	1.249	0.319		0.296	0.246
Glu225+Tol	#20		1.430	0.227	1.245	0.320		0.349	0.575
Glu225+Bz	#23		1.455	0.224	1.240	0.341			1.620
Glu225+C10	#33		1.442	0.234	1.316	0.332			
Glu225+C7	#27		1.436	0.241	1.310	0.362			
Glu225+C5	#30		1.455	0.243	1.401	0.461			
502+Glu	#14	0.782	2.970	0.228	0.631	0.177	0.068		
502+Glu+TMB	#15	0.413	2.318	0.188	0.622	0.171	0.081	0.565	0.201
502+Glu+Xyls	#18	0.559	2.560	0.205	0.623	0.176	0.051	0.303	0.287
502+Glu+Tol	#21	0.552	2.522	0.213	0.636	0.191	0.051	0.441	0.733
502+Glu+Bz	#24	0.653	2.709	0.205	0.618	0.193			1.612
502+Glu+C10	#34	0.740	2.943	0.237	0.673	0.190	0.067		
502+Glu+C7	#28	0.740	2.936	0.229	0.746	0.245	0.065		
502+Glu+C5	#31	0.747	2.935	0.227	0.826	0.363	0.071		